Chemical Manipulation of Polyhedral Oligomeric Silsesquioxanes for the Synthesis of Modular Materials and Catalysts

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Declarations

I, Bruce William Manson, hereby certify that this thesis has been composed by myself, that it is a record of my work and that it has not been accepted in partial or complete fulfilment of any other degree or professional qualification.

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I was admitted to the Faculty of Science of the University of St. Andrews under the Ordinance General No. 12 on the 6th January 1998 and as a candidate for the degree of Ph.D. on the 6th January 1999.

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Courses Attended

The Department of Chemistry requires that a number of lecture courses be attended by postgraduate students. The courses attended by this student were: "Crystallography" (Dr P. Lightfoot), "NMR for Synthetic Chemists" (Dr C. Wheeler), Radical Chemistry" (Dr. Nonhebel), "Applications of NMR Spectroscopy", "Advanced Inorganic Electrochemistry" (Dr. J. Crayston) and "Hot Topics in Catalysis" (Prof D. J. Cole-Hamilton and Dr P. A. Wright).

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Contents

Abbreviations and Symbols

AIBN	Azo-isobutyronitrile
BET	Brunauer Emmet and Teller surface area analysis
Bp	Boiling point
CPMAS	Cross polarisation magic angle spinning
°C	Degrees celsius
d	Doublet
Dec	Decomposed
δ	Chemical shift
DMF	Dimethylformamide
DMSO	Dimethylsulphoxide
DPMAS	Direct polarisation magic angle spinning
FTIR	Fourier transform infra-red spectroscopy
GC/MS	Gas chromatography mass spectrometry
HMPA	Hexamethylphosphoramide
Hr	Hours
HRMS	High resolution mass spectrometry
IR	Infra-red
J	Coupling constant in Hertz
LDA	Lithium diisopropylamine
m	Medium (for FTIR data)
	Multiplet (for NMR data)
M	Moles per litre
M+	Mass of molecular ion

Min	Minutes
Mp	Melting point
MS	Mass spectrometry
M/z	Mass to charge ratio
NMR	Nuclear magnetic resonance
Platinum (dvs)	Platinum divinyltetramethyldisiloxane complex
POSS	Polyhedral Oligomeric Silsesquioxane
PSU	Primary building unit
PXRD	Powder X-ray diffraction
s	Singlet (for NMR data)
	Strong (for FTIR data)
SBU	Secondary building unit
t	Triplet
THF	Tetrahydrofuran
TLC	Thin layer chromatography
UV	Ultra-violet
vs	Very Strong
vw	Very weak
υ_{max}	Infra-red absorption frequency
w	Weak
XRD	X-ray diffraction

Abstract

A study has been undertaken to investigate the chemical modification of near cubic polyhedral oligomeric silsesquioxanes (POSS) of the general formula $[RSiO_{3/2}]_8$ to produce molecular building blocks suitable for the preparation of microporous modular solids with engineered properties. Several approaches have been taken in an effort to prepare octa-functional POSS suitable for self-assembly resulting in the synthesis of new benzoic acid functionalised POSS and, preliminary analysis suggests, two new highly functionalised pyridine bearing POSS. Studies into the use of Heck type arylation, the Gabriel synthesis and thyl radical reactions to modify functionalised POSS have also been undertaken with a view to identifying new synthetic routes to functionalised POSS.

During efforts to investigate the requirements for the preparation of porous materials from POSS, several new copolymers were prepared through hydrosilylation of POSS only and POSS-spacer mixtures. Three of these copolymers are porous in nature and have high surface areas measuring several hundred meters square per gram. Acid cleavage has been used to alter the form of one of these copolymers by, it is suggested, opening individual POSS within the structure of the material. This demonstrates that it is possible to modify linked POSS molecules in a manner and may provide a route to catalytic materials from POSS copolymers and, potentially, extended networks of POSS.

Chapter 1 Introduction

1.1 General Introduction

In recent years, molecular sieves such as zeolites and other inorganic oxides[1, 2] have become increasingly important in catalysis and size selective applications.[3] Materials of this type are extremely useful in catalysis due to their large surface area and, more importantly, their capacity for size and shape selection during catalytic processes. Although the preparation of these materials has been studied for many years, the mechanisms by which they form are still poorly understood making it difficult to prepare materials tailored for specific applications.[4]

Alternatives to these molecular sieves have been developed and are generally based on organic/inorganic hybrid systems.[5, 6] These materials offer several advantages over inorganic oxide molecular sieves in that they can be prepared under very mild conditions and their preparation is both more readily understood and controlled. They also have several disadvantages however, the most important of which is their amorphous nature.

Due to the problems associated with the established microporous solid types and their preparation, the objective of this project has been to develop a system or systems which can offer a viable alternative to the existing techniques. In an effort to achieve this goal, a molecular building block approach was taken with functionalised polyhedral oligomeric silsesquioxanes serving as the building blocks. By linking these units together, it was hoped that porous modular materials[7] with well defined

structures could be prepared with properties determined by their precursor building blocks. Once methods had been developed to prepare porous solids, a means to convert them into catalytically active materials was to be sought with a view to preparing materials with comparable utility to those already available.

1.2 Porous Materials

A wide variety of porous materials have been discovered and developed with wide ranging properties governed by their particular form and composition. Porous organic,[8] inorganic[1, 2, 3, 4] and organic/inorganic hybrid[5, 6] solids have all been documented, including both amorphous and highly ordered materials. The current range of readily available porous materials allow a wide range of pore structures, diameters and volumes to be accessed, sometimes even within one material.

IUPAC convention currently describes materials with pore diameters below 5 Å as nanoporous, between 5 and 20 Å as microporous and above 20 Å as mesoporous. Although nanoporous and mesoporous materials have their applications,[9] only microporous materials were considered in this project. Microporous materials allow molecular recognition down to a resolution of less than 1Å and are therefore of great industrial importance.[4]

Molecular Sieves

The term molecular sieve refers to a class of porous materials with very well defined crystalline structures and porosities that are typically in the micropore region.[1] They are referred to as molecular sieves due to their molecular recognition properties which allow them to segregate atoms and molecules on the basis of their physical properties such as size and charge.[10] A number of sub-categories of material can be identified including types such as silicas, aluminophosphates and metalloaluminates.

The silica group contains further sub divisions but probably the most well known are zeolites. First recognised as a new class of materials by A.F. Cronstedt in 1756,[11] zeolites are now generally regarded as the epitome of microporous materials. They are comprised of silicon and aluminium oxides forming intricate porous structures. These materials can be found naturally but synthetic techniques have been developed to allow artificial zeolites to be produced and a large number of zeolitic materials are now available, each with a distinct structure.

The structures of zeolites and the majority of molecular sieves are based on linked TO_4 tetrahedra where T is a tetrahedral atom such as, in the case of zeolites, silicon or aluminium. These tetrahedra make up the basic structure of these materials and can be described as their primary building units (PBUs). Although the structures of these materials can appear complex, they can be viewed as being comprised of small units referred to as secondary building units (SBUs) which are in turn comprised of PBUs (***Figure 1.1***). Despite the range of structures which are known to

exist in microporous materials, only a small number of SBU patterns are required to define all of the known zeolite and molecular sieve types.

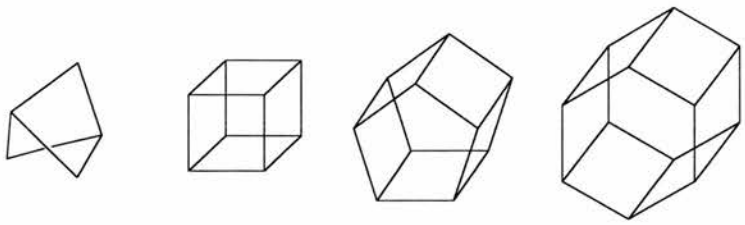

Figure 1.1. *Examples of secondary building units found in zeolites. From left to right, 4-1 breached ring, 4-4 double ring (double four ring), 5-5 double ring and 6-6 double ring.*

Zeolites have the general formula $M^{n+}_{x/n}[(AlO_2)_x(SiO_2)]^{x-}\cdot zH_2O$ where M is a cation. Cations are required within zeolites and similar materials to offset the negative charge associated with the tetrahedra. They do not actually form part of the structural fabric of these materials but reside externally to the linked tetrahedra in the cages and channels formed by them. Initially, only alkali metal cations were used in the preparation of zeolites which restricted the composition of these materials, but it has been found that organic cations can also be used which has give a greater degree of flexibility in the composition of the materials formed.

Early attempts to prepare artificial zeolites involved the use of high temperatures and pressures in an effort to simulate the conditions that these materials were expected to form under in nature. It has since been demonstrated that such conditions are not required and zeolitic materials are now routinely prepared using hydrothermal techniques at temperatures ranging from 100 to 250 °C under highly alkaline conditions and autogenous pressure.

Aluminophosphates are another major molecular sieve group and were first prepared by Wilson *et al* in 1982.[4] They have the general formula $Al_2O_3 \cdot 1 \pm 0.2P_2O_5 \cdot xR \cdot yH_2O$, where R is the amine or quaternary ammonium salt used in their preparation, which gives them a structure based on aluminium and phosphorous rather than the silicon-based structures of the silica group. Again, hydrothermal techniques are used to prepare these materials but unlike zeolitic materials, these are prepared under either neutral or mildly acidic conditions. Replacing P^{5+} and Al^{3+} ions within the structure with metal cations results in the preparation of metal aluminophosphates while replacing them with silicon results in the prepration of silicon aluminophosphates which comprise further sub-divisions of this group of materials. A wide variety of metals have now been incorporated into this type of material, including vanadium, cobalt, indium and gallium.

Other molecular sieve groups include materials such as germanium aluminates and gallogerminates but these are analogous to those discussed above albeit with different chemical compositions.[1]

Although the preparation of molecular sieves, particularly zeolites, has been studied for some time now, the mechanisms involved are poorly understood. The formation process can be viewed simply as the dissolution of the solid reactants, small scale ordering of the reactants to form nucleation sites and then the growth of these nucleation sites to form the structure of the material.[4] Detailed understanding of these stages has not yet been achieved but it is recognised that both thermodynamic and kinetic effects contribute to the form of the final material. The typical hydrothermal

synthesis used to prepare these materials contains a large number of variables ranging from the inorganic ion source through to the reaction temperature, with each variable having the potential to alter the reaction kinetics. Due to the large number of variables associated with the synthesis of these materials and the effect that changing any one of these has on the progress of the reaction, new molecular sieves are generally prepared through a systematic variation of reactants and reaction conditions for a given system.

Despite the complex nature of the reaction mechanisms, trends have been recognised such as smaller pore sizes generally being obtained when higher reaction temperatures are employed. Although observations of this type can assist in the preparation of new molecular sieves, they do not facilitate the rational preparation of materials to suit specific applications. This means that although they have numerous industrially important applications because they are well suited to molecular recognition and their compositions can give them catalytic properties, it is extremely difficult to rationally prepare materials of this type that have properties tailored to a specific application. This has resulted in a great deal of research effort being applied to either develop an understanding of the mechanisms involved in molecular sieve formation or to find alternative approaches for preparing well-ordered microporous materials with and without catalytic properties.

Organic/Inorganic Hybrids

The sol-gel polymerisation of trimethoxy- and triethoxysilane[5] can be used to prepare porous amorphous silicas. This process involves the acid- or base-catalysed

hydrolysis of the alkoxysilanes followed by their condensation to form oxygen linked silicon networks. Although the simplicity of this system restricts the range of materials that can be produced, varying the reactants and the conditions can allow a degree of control over the nature of the products formed.

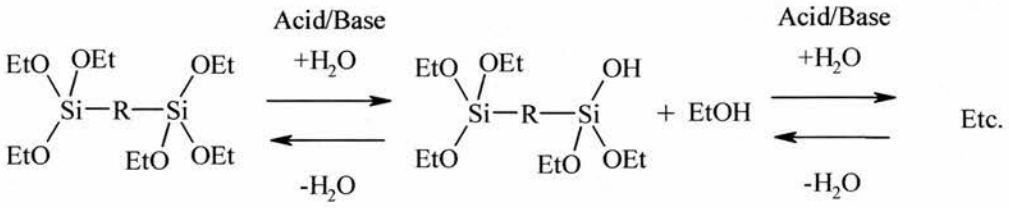

Figure 1.2. *Hydrolysis of triethoxysilanes containing organic component R where R could be an alkyl chain, aryl group, etc.*

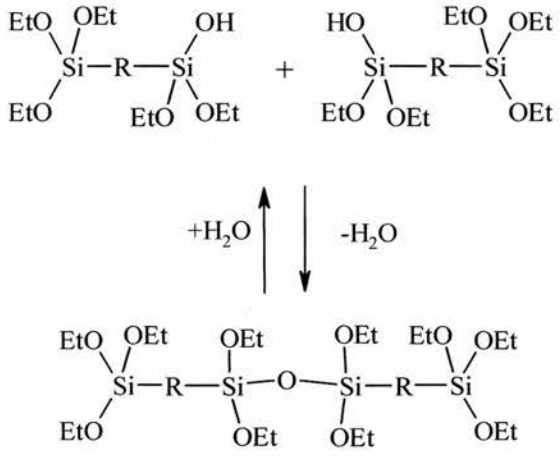

Figure 1.3. *Condensation of hydrolysed triethoxysilanes containing organic component R where R could be an alkyl chain, aryl group, etc.*

By introducing organic components into silanes present in sol-gel reaction mixtures (***Figures 1.2 and 1.3***), a greater degree of control over the properties of the materials formed can be exerted, with the starting materials having considerable influence over the nature of the product. In addition to greater control of the reaction,

the introduction of the organic components, especially groups such as aromatic rings, produces materials with much higher degrees of porosity than simple silanes.[5]

One major drawback to this technique is that the structure can shrink or collapse on drying and techniques such as supercritical drying must be employed if the highest surface areas are to be obtained. In addition, these materials are amorphous in nature and therefore lack the precisely controlled pore structure of zeolites and other molecular sieves. Materials in the micropore region can be prepared by this type of reaction but, due to the lack of order in these materials, there is typically a spread of pore sizes. A further problem with this type of system is the large number of unreacted hydroxyl groups which remain after formation because of the geometric constraints placed upon the forming polymer. Without further reaction, these groups can give the resultant material undesirable hydrophilic properties.

Recently, polyhedral oligomeric silsesquioxanes have been copolymerised to produce porous inorganic/organic hybrids with high surface areas.[6] These materials are similar to sol-gel polymers in that they lack order in their structure and can contain a wide variety of pore sizes and geometries. They can however give access to pores in the micropore region, offer a shorter formation time, contain no residual hydroxyl groups and are subject to less shrinkage on drying. These materials are discussed in greater depth below (**Section 1.6**) and will not therefore be considered further here.

Modular Materials

An emerging area in the field of porous solids is the creation of modular materials with porous structures. Modular materials[7] are composed of molecular building blocks which are interlinked to form the bulk material. Through careful selection of the geometry of the building units, it is possible to prepare structures with a porous nature. These materials are discussed in greater depth later in this chapter (**Section 1.3**) and will not therefore be considered further here.

Applications

Inorganic oxide molecular sieves are widely used, particularly in industry and have found many applications. At a relatively simple level, this type of material has been used in applications such as selective absorption where it is their well defined pore structures provide the all important selectivity.[12] Not only do the size of the pores control the behaviour of the material, but their shape can also contribute to selectivity. They have also been used in chemically active roles in catalysis where their Lewis acid properties are of key importance. Two examples are olefin epoxidation[13] and hydrocarbon cracking,[14] both of which are industrially important although inorganic oxide molecular sieves have many more uses in catalysis. Again, both the pore size and shape within the materials determine how they will perform, often offering very selective catalytic properties. Due to the presence of counter ions within the pores and channels of inorganic oxide molecular sieves, these materials can also lend themselves to ion exchange applications.[15] As the counter ions are not irreparably bound to the structure of the solid they can be manipulated with relative ease.

Inorganic/organic hybrids have also found or have been proposed for numerous applications but as these materials have only been developed relatively recently many as yet unidentified applications may still be proposed. With suitable organic components located within the fabric of the material, hybrids prepared through sol-gel techniques can be used to separate mixed gases. A typical example is the hybrid prepared by Kuraoka *et al* which incorporates N,N'-disalicylideneethylenediaminato)cobalt(II) and N-vinylpyrrolidone as a mediation agent.[16] This particular material has a high oxygen selectivity which allows it to act as a filter and separate oxygen from other gases such as nitrogen. Similarly, the ability to control the pore size and structure as well as surface properties of inorganic/organic hybrids makes them suitable for use in ultrafiltration membranes.[17]

In addition to materials separation, inorganic/organic hybrids have also found novel applications based on their porous nature. Under the mild conditions generally used in the preparation of hybrids, organic components in the reaction mixture can retain many if not all of the characteristics they had before they were incorporated into the final matrix. This allows dye molecules containing chromophores to be incorporated sol-gel preparations to produce materials that can be used in lasers, waveguides, nonlinear optics and similar applications.[18] Dried xerogels can be treated with components such as aqueous $CdSO_4$ and Na_2S to produce semiconductor particles, CdS in this example, within the matrix.[19] Although there is only a rough correlation, it has been observed that the size of these particles is dependent on the pore size of the xerogel offering an element of control over the process. The molecular sieving properties of hybrids with well defined pore size distribution can be

used to enhance chemical sensors.[20] By placing a thin film of this type if material over the sensor, the range of molecules reaching the sensor itself can be reduced making much higher levels of sensitivity possible. The low density structure of these materials, their insulating properties and the variety of building units that can be incorporated into them also make them ideally suited to applications in electronic devices as dielectric materials.[21]

Many more applications for microporous materials have either been found or suggested and those described above should be viewed as an indication of the importance of these materials and not an exhaustive list of applications.

Project Objectives

Microporous materials have many applications and are becoming increasingly important in industry, but the established technologies, although extremely useful do have distinct disadvantages.

Molecular sieves are a well-proven technology and have precisely defined structures offering the potential for very accurate molecular recognition. The preparation of new materials of this type however, is largely through the systematic progression through various reaction mixtures and conditions.

Sol-gel reactions can prepare high surface area materials with the nature of the reactants offering a degree of control over their pore sizes and internal architecture. Sol-gel polymerisation is relatively simple to understand but does not offer the

precisely defined structures observed in zeolites and molecular sieves. High surface areas can be obtained, but these often require the application of techniques such as supercritical drying to be achieved. In addition, a large number of hydroxyl groups are left behind in the resultant materials giving them hydrophilic properties.

The preparation of porous copolymers from silsesquioxane precursors is a recent development but it has been recognised that these materials may be used in applications which currently make use of sol-gel type materials but without the drawbacks of hydrophilicity and long preparation times. These materials may also lend themselves to the preparation of catalytically active materials through modification of their structures, their precursors or of their unreacted groups (**Section 1.7**). This type of material does however suffer from the draw backs of having a poorly ordered structure and a range of pore sizes.

Porous networked solids are still a relatively new area of research and have not yet been fully exploited. To date, only relatively simple building blocks have been used to create porous modular materials which restricts the range of materials that can be prepared. Although in principle this technique allows for a very flexible approach to be taken to the preparation of porous materials, suitable building blocks must be prepared to achieve this.

Currently available microporous materials are lacking in several respects and there is a need for a system for the preparation of porous materials with well-defined structures but at the same time through a mechanism that can be readily understood and controlled. In addition, such a system should be capable of producing a range of

materials with properties that can be tailored to meet specific requirements. This does not necessarily mean that materials meeting these requirements would be prepared initially but that the system could be controlled to ultimately yield the desired material in a rational manner. Although the preparation of porous modular materials has not yet reached an advanced stage of development, this approach could allow many of the problems associated with current porous systems to be overcome and was selected as the basis for this project.

1.3 Modular Materials

Modular materials, sometimes described as network solids, are solids which are prepared from discrete units, commonly referred to as molecular building blocks, which are linked together in a controlled manner.[7] The linking mechanisms employed to prepare these materials are non-covalent which facilitates controlled manufacture allowing well-defined materials to be prepared. Materials such as copolymerised silsesquioxanes could be viewed as being modular materials as they are prepared from discrete building block type units but such systems may be better described as polymers or copolymers and will not therefore be discussed here.

Molecular building blocks can take many forms, but they all have components which can allow them to be linked together in a particular order. These components usually take the form of functional groups terminating in a unit appropriate to the selected linking mechanism. Typical methods used to link molecular building blocks together include hydrogen bonding, metal co-ordination and weaker bonding such as

π-π interactions. Although these are probably the most commonly used methods, almost any technique used in crystal engineering should be applicable as long as appropriate building blocks can be prepared.[21]

The act of bringing together numerous components to assemble a larger form is a complex, technically demanding task. The orientation of the building blocks and their linking groups must be controlled to allow them to come together in the desired manner and the linking process must be reversible to allow misalignments to be rectified. Self assembly is therefore required in these materials and this can be achieved through the use of components with characteristic features such as charge or shape and reversible linking mechanisms such as those described above. It should also be borne in mind that while the molecular building blocks and the techniques used to bring them together must encourage the preparation of well-ordered structures, they must also discourage interpenetration of the structure.

The use of molecular building blocks has been demonstrated on numerous occasions in the preparation of one, two and three dimensional materials and structures.[22, 23, 24, 25, 26] The nature of the solid produced depends on the building blocks used and the method employed to link them. Species such as bi-pyridines can be linked through metal centres resulting in a one dimensional ribbon product due to the bi-functional nature of the bi-pyridine building blocks.[27] Tri-functional molecules such as benzenetricarboxylate can form two or three dimensional extended structures depending on the techniques that are applied.[28, 29] The manner in which the building blocks are linked can also determine the nature of the solids prepared from them. An example of this is the metal co-ordination of cyanoisocyanoarenes where different

metal species co-ordinate different numbers of the aryl building blocks to produce one, two or three dimensional structures.[30] The building block approach can also be applied to tetra functional molecules and highly functionalised units such as the alcohol bearing cubic polyhedral oligomeric silsesquioxane prepared by Roesky *et al.*[31] Although they were not aiming to produce a modular solid, this octa-functionalised molecule crystallised through hydrogen bonding producing a weakly linked three dimensional extended network.

If appropriate units are selected, it is possible to prepare well-defined three dimensional porous structures using a building block approach. A well-documented example of this is the porous material prepared from benzene tricarboxylate by Yaghi *et al* (***Figure 1.4***).[29] The material was prepared using zinc (II) to link de-protonated carboxylic acids groups of the aryl building block. The pores within this material can be accessed and it's structure is relatively robust, which suggests that it may be possible to find practical applications for it.

Different approaches can be taken to prepare modular materials, but the arrangement of the molecular building blocks is generally achieved through self-assembly. For example, room-temperature processes can make use of diffusion or evaporation to gently drive the process of self-assembly. In the case of evaporation, the components of the modular solid are free too move in the solution but as the volume of the liquid decreases, the components are forced together and, in theory, move towards the most stable form.

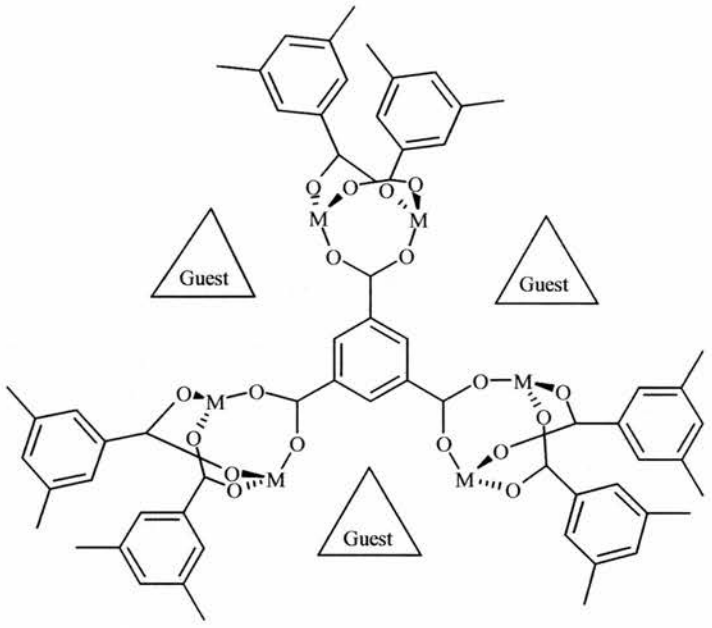

Figure 1.4. *Schematic for a portion of the three dimensional structure assembled by Yaghi et al from benzene tricarboxylic acid and zinc (II). M indicates the metal species while the "Guest" units indicate solvent molecules within the structure.*[29]

Alternative approaches include the use of hydrothermal or solvothermal techniques.[32, 7] In these particular examples, materials which can be readily linked through non-covalent bonding or metal co-ordination are combined under elevated temperatures and pressures to produce well-ordered materials. Under these conditions, numerous transitionary states or forms can be sustained, allowing the modular material to move into a more thermodynamically stable state. With the correct selection of building blocks, this stable state should take the form of a well-defined material.

One of the principle advantages of this approach to preparing solids is that the integrity of the building blocks is maintained as the material is being assembled. This

confers properties on the resultant solid which are derived, at least in part, from the building blocks employed.[7] This can provide great control of the properties of these materials and may allow materials to be designed for particular applications. In addition, the assembly of these materials is thermodynamically driven, making it much easier to understand the mechanisms at work during this process.

Project Application

As a modular approach to the preparation of solid materials offers a high level of control over the nature of the material produced, an assembly mechanism which is relatively easy to understand and a route to porous materials, this project has aimed to take this approach. The nature of the building blocks to be used was recognised as being key to the success of the project and functionalised polyhedral oligomeric silsesquioxanes were selected for this role. This type of molecule has a three dimensional geometry and can be functionalised with a variety of groups making them ideal for this type of application.

1.4 Polyhedral Oligomeric Silsesquioxanes (POSS)

Polyhedral Oligomeric Silsesquioxanes (POSS) are multifunctional molecules with a cage-like core of oxygen bridged silicon atoms formed through hydrolytic condensation (***Figure 1.5***).[33, 34, 35] These molecules have the general formula $[RSiO_{3/2}]_n$ where the value of n (always even) determines the size of the silicon-oxygen network with the lowest value being 6. Attached to each silicon atom within

the molecule are functional groups, R, which can range from hydrogen through to complex multi-atom groups.

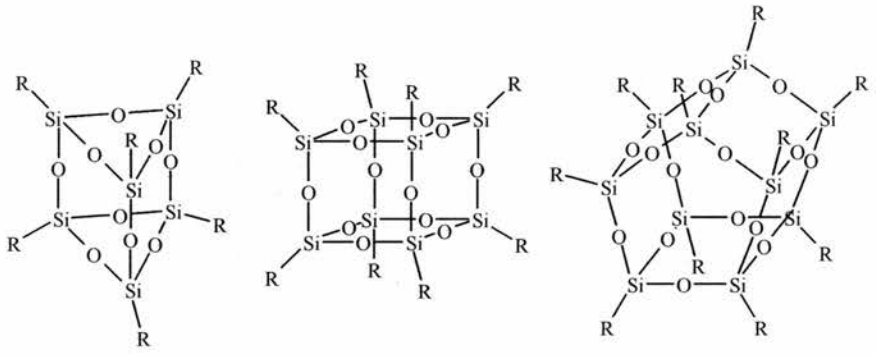

***Figure 1.5**. From left to right, sketches of POSS with n values of 6, 8 and 10. Note: These sketches are intended to only be indicative of the approximate structures of these molecules and do not accurately reflect the bond angles between the silicon and oxygen atoms.*

Although misidentified, POSS were first prepared by Ladenburg in 1875 during experiments involving condensation reactions.[36] A subsequent study by Meads and Kipping investigating the hydrolytic condensation of silanes led them to the conclusion that such reactions were of little use as they produced complex mixtures of materials.[37] Meads and Kipping reported their findings in 1915 but it was not until the 1950s and 1960s that further work into the controlled preparation of POSS made appreciable progress.[38, 39, 40] Since then, a large number of functionalised POSS have been developed ranging from POSS bearing only hydrogen[41] through to POSS with functional groups so large that they cease to be referred to as POSS molecules and are more appropriately described as dendrimers[42] and POSS bearing metal species.[43]

Depending on the value of n, various geometries of POSS can be prepared, often in the same hydrolytic condensation.[41, 44, 45] POSS with values of n of 6 and 8 have just one structural isomer each, but larger POSS can have several isomers. Although POSS with differing n values may have similar properties, the differences between them are relatively easy to detect. NMR spectroscopy can indicate what type of silicon-oxygen core functional groups are attached to through differences in chemical shift,[45] while IR spectroscopy[41] and XRD[38] can pick out differences in structure. For convenience the different POSS geometries can be described by the term Tn where the T originates from the three oxygen atoms bound to the silicon i.e. the silicon is tri-substituted. T8 POSS were selected for this project as they are relatively easy to prepare, have a very desirable geometry and can only be prepared as one isomer.

T8 POSS are usually referred to as cubic in form but this only refers to their general shape as their sides are slightly distorted due to the strained nature of this configuration. Fully formed, the silicon-oxygen core of this type of molecule has a diameter in the region of 3-4Å.[6] Although sensitive to bases and strong acids, POSS are very stable molecules and can retain their silicon-oxygen network at temperatures above 400 °C.[46] The organic groups attached to the core tend to be the weak points of these molecules with their break down or degradation occurring at much lower temperatures than that of the core.

POSS are closely related to polyhedral silicates but lack the oxygen atom between the silicon-oxygen core and the functional groups attached to it.[47, 48, 49] From the perspective of this project, this oxygen atom would introduce an undesirable

flexibility to any silicate building blocks, defeating the principle aim of this project which was to produce well ordered materials. In addition, it was expected that the use of silicates in networked and copolymerised structures would prevent the effective conversion of these materials into catalysts *via* acid or base cleavage (**Section 1.7**).

POSS Synthesis

The silicon-oxygen core of cubic POSS molecules can be prepared in several ways, but all involve hydrolysis of a silane bearing three hydrolysable functional groups and a fourth non-hydrolysable group.

The addition of trichlorosilanes to a water-containing solution results in rapid hydrolysis of the silane. The resulting silanols then go on to form the silicon-oxygen core of the POSS molecule through condensation reactions which also generate numerous by-products. During this process, the non-hydrolysable groups remain intact and are retained at the corners of the resultant POSS. Depending on the functional group type, the condensation process can be performed at room temperature[50] or the reaction may require elevated temperatures.[46] It should be noted that although hydrolysis step can be performed with little or no solvent other than the reactants themselves, solvents are required to avoid the preparation of intractable gels and promote the formation of polyhedral structures.[38]

Trialkoxy silanes can also be hydrolysed to prepare POSS in a similar manner to trichlorosilanes.[51] Although the process of POSS formation is similar, the alkoxy

groups are less reactive than chloro groups and hydrolysis requires acid or base catalysis.

Scarce water hydrolysis can provide an alternative to hydrolysis using "bulk" water reactions. No water is added to the reaction mixture but it is generated in situ through reactions such as the sulfonation of an aryl component in the reaction mixture or a partially hydrated metal salt solution. Control of the volume of water present in the reaction mixture can result in a more controlled reaction and higher yields of the desired product.[41, 45]

The products formed in these reactions depend greatly upon the nature of the functional group attached to the silane. For example, in the case of 4-chloromethylphenyltrichlorosilane, hydrolytic condensation with water in acetone produces only T8 POSS while scarce water hydrolysis of trichlorosilane produces a mixture of T8 and T10 POSS. Conditions and reactants can be optimised to produce sphereosilsesquioxanes, partially formed POSS and other species, but this project was focused primarily on T8 POSS.

Preparation of Functionalised POSS Cubes

To allow POSS cubes to be used as molecular building blocks, appropriate functional groups must be attached to their silicon atoms. The preparation of POSS functionalised with organic and mixed organic/inorganic groups has been well documented and many examples of functionalised POSS have been reported. A range of different strategies have been used to prepare functionalised POSS, but these can

be divided into two principle approaches, direct hydrolytic condensation and synthetic manipulation of pre-formed POSS.

Functionalised POSS can be formed directly through the hydrolytic condensation of trifunctional silanes bearing the appropriate non-hydrolysable group. Numerous examples of this have been reported, ranging from simple vinyl functionalised molecules[50] to those bearing aromatic systems.[52]

The main advantages of this approach are that the POSS are effectively formed in a single reaction step and only the desired functional groups are present in the reaction mixture. This means that the POSS which are produced are functionalised with only the intended functional group unless side reactions modify this group. In addition, the reaction by-products can be readily separated either through recovery of the product by filtration[46, 50] or by making use of the physical differences, such as solubilities,[45] of the POSS formed. Preparation of the desired group as a component of a mono-silicon system is also beneficial as it allows techniques which could destroy the fabric of the POSS core to be employed and allows preparation of the group without any interference from the core.

The draw-backs of this technique are that low yields are generally obtained, particularly from complex silanes,[46] and appropriate silanes must be synthesised to produce the desired POSS. It may not always be possible to prepare suitable silanes as the non-hydrolysable functional group must be capable of surviving the hydrolytic condensation process and must also be immune to the relatively reactive hydrolysable groups also bound to the silane.

Although the silicon-oxygen core can govern the behaviour of the functional groups attached to it, these groups can still be synthetically manipulated, offering a method of functionalised POSS preparation that complements direct hydrolytic condensation. Once a suitable precursor POSS has been hydrolytically condensed, it's functional groups can then be modified using a wide range of synthetic techniques although several are particularly useful for POSS systems.

Hydrosilylation is the reaction of a silicon hydride group with a carbon-carbon double bond resulting in the formation of a carbon silicon bond. This reaction can be initiated at very high temperatures, [53] but is it is generally catalysed under mild conditions using complexes of platinum, palladium or rhodium.[54] Platinum catalysts have been found to be active in the majority of cases and two forms in particular, Spears catalyst (chloroplatinic acid)[55] and Kharstedt's catalyst,[56, 57] have been found to be highly effective. Chloroplatinic acid is a simple but effective platinum (IV) catalyst which can be used to perform very selective hydrosilylations. Kharstedt's catalyst is a title given to several highly effective platinum (0) complexes with similar properties and structures. Platinum dimethyltetravinyldisiloxane complex typifies this type of catalyst where the platinum is co-ordinated between olefin groups which act as a support for the system.

Hydrosilylations are generally high yielding and have been used to link silicon hydrides bearing POSS to straight chain alkenes[58], allyl siloxanes,[59] allyl nitriles,[60] allyl epoxides,[60] unsaturated esters,[61] vinylferrocene,[62] phenyl alkenes,[58] unsaturated silanes,[63, 64] and unsaturated alcohols.[31] Although the POSS used in hydrosilylation reactions tend to be of the hydrido type, vinyl functionalised POSS are also

commonly used but these require the other reactant to be a silane with a silicon hydride group. This is particularly useful when a chlorosilane functionalised POSS is required as an intermediate species in a reaction scheme.[42, 65] These are not exhaustive lists of these types of reaction, but serve to give an indication of the utility of this technique.

Metal catalysed hydrosilylations are particularly useful in that they generally proceed under mild conditions which are not aggressive to silicon-oxygen networks. As well as being high yielding, under the correct conditions these reactions can be very selective with respect to the carbon atoms of the olefinic group.[42, 65] They are particularly useful reactions for POSS chemistry as both hydrido[45] and vinyl[50] functionalised POSS can be readily prepared in yields which exceed those obtained during the preparation of more complex POSS. In addition, vinyl and hydrido silanes are generally simple to prepare and make ideal reaction partners for appropriately functionalised POSS.

As well as hydrosilylation reactions, the reaction between chlorosilanes and metallated species is used regularly in POSS chemistry. Grignard reagents and lithiated species can readily combine with chlorosilanes whether these are discrete silanes or chlorosilane groups attached to POSS.[64, 65] With the availability of substrates such as dimethyl chlorosilane, metallated species can be easily converted into silanes suitable for hydrosilylation to appropriately functionalised POSS. Alternatively, chlorosilanes can be hydrosilylated to POSS and the metallated species reacted with the chlorosilane bearing POSS.

Another type of reaction which has been used routinely in POSS chemistry is cross metathesis.[66] This technique essentially involves an exchange of functional groups between vinyl bearing POSS and olefinic molecules. Although not used in this project, cross metathesis has been used frequently in the preparation of hard blocks for incorporation into modified polymers.

Many techniques used in general synthetic chemistry may have applications in the modification of functionalised POSS (***Figure 1.6***). Vinyl bearing POSS have been reacted with m-chloroperoxybenzoic acid to produce epoxide bearing molecules.[67] Aryl functionalised POSS have been catalytically hydrogenated to convert them to their aliphatic form.[52] Chloromethylphenyl functionalised POSS have been converted to alcohols *via* a reaction with silver perchlorate.[46] Again, this is not an exhaustive list of reactions that have been performed on preformed and previously modified POSS molecules, but gives an indication of the range of manipulations which can be achieved.

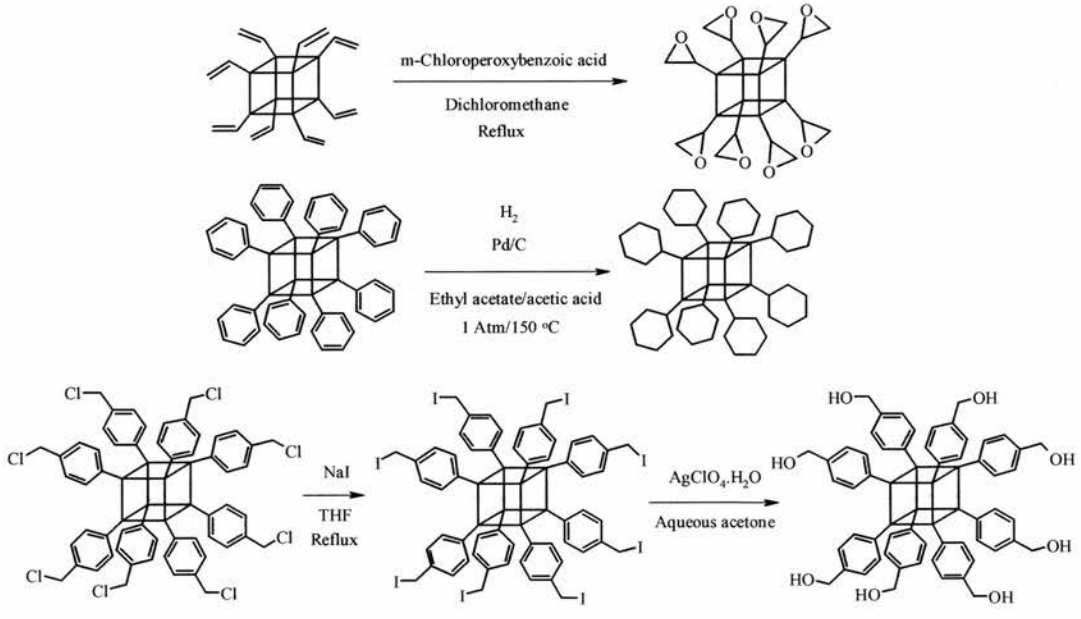

Figure 1.6. *Three examples of synthetic manipulation of pre-formed POSS.*

The cores of POSS molecules have a strong electron-withdrawing effect on the functional groups bound to them and this should be recognised when attempts are being made to modify them.[46] With spacer units between the core and reactive element of the functional group, this effect can be reduced allowing 'normal' synthetic techniques to be employed. This is not a problem in applications such as dendrimer chemistry, but when attempts are being made to produce POSS suitable for self-assembly, long pendent arms are not desirable. Another problem encountered when attempting to modify POSS is the susceptibility of the core to cleavage by basic solutions, strong acids and, it has been suggested, amines.[68] These can restrict the range of synthetic options available when attempting to manipulate a POSS system and necessitate careful planning of synthetic strategies.

The synthetic manipulation of pre-formed POSS offers some distinct advantages over direct hydrolytic condensation. The POSS that are manipulated can be relatively simple functionalised POSS which means that the yield of the hydrolytic condensation is likely to be higher than that expected from a similar reaction using a silane functionalised with a complex group. This also means that appreciable quantities of silanes which may be difficult or expensive to prepare do not have to be sacrificed in low yielding hydrolytic condensation reactions. This approach need not employ chlorosilanes or alkoxysilanes therefore functionalities which are susceptible to these groups or the conditions and materials encountered during hydrolytic condensations can be prepared. Synthetic modification also allows components to be prepared and purified before they are added to the POSS species through techniques

such as hydrosilylation resulting in a reduction in the number of unwanted groups bound to the POSS.

Synthetic manipulation can be problematic however, as the use of alkalis and strong acids can damage the silicon-oxygen network at the core of the POSS which restricts the range of synthetic techniques that can be applied to POSS. Another major problem is that reaction yields may be too low to produce fully modified POSS. As POSS have effectively eight reactive sites bound to the core, it will not be possible to separate modified functional groups from unreacted groups if there is an even distribution of reaction across all of the POSS. For example, if a reaction gave a yield of 50 % and this was distributed across all of the POSS, then it would be expected that four of the functional groups bound to each POSS would react while the other four would not but it would not be possible to separate the reacted and unreacted groups as they would all be bound to the same molecule.

Throughout this project, a range of approaches were taken to producing functionalised POSS, including both direct hydrolytic condensation and synthetic modification of pre-formed POSS. Hydrosilylation and metallation were used, but synthetic techniques that had not previously been reported as being applied to POSS were also investigated with a view to identifying potentially useful techniques.

Applications for POSS

The number of applications for POSS molecules, both realised and proposed, is steadily increasing and with the number of research groups currently studying

POSS molecules, it is anticipated that this will continue to increase. Due to their unique form, POSS lend themselves to a wide variety of applications based on their physical properties and their multiple functional groups.

POSS systems can be used as models for silica systems due to their similarity to crystalline frameworks found in materials such as zeolites. Their rigid form renders them ideal for modelling silica surfaces[69] and partially condensed POSS can act as hydroxylated silica surface sites.[70] This allows metal species to be introduced to form materials with catalytic properties (**Section 1.6**).

POSS cubes make ideal candidates for the cores of dendrimer type catalysts due to their eight functional groups.[42] Highly functionalised convergent and divergent dendrimers have been prepared and studies are ongoing into their use as catalyst supports. As the cores of these molecules branch in 8 directions, a highly functionalised outer sphere can be prepared in only a few synthetic steps. The principle advantage of these systems is that they will be small enough to behave in a manner similar to that of homogenous catalysts but will be large enough to be recovered using ultrafiltration techniques in a manner similar to that employed for heterogeneous catalysts.

POSS have also found applications in the preparation of polymeric materials. Due to their multifunctional nature, they are ideal cross linking agents[71] but can also be used as hard blocks to modify the properties of polymeric materials[72, 73] or can be used to prepare homopolymers and copolymers.[74, 75] When used as hard blocks, a functional group is used to link the POSS to the fabric of "conventional" polymeric

systems. This can introduce enhanced mechanical properties into these materials including increased temperature stability and resistance to UV light. Enhanced thermal stability has led to the creation of materials which can be used as fire retardants and polymeric materials which can be used in components for rocket motors. Porous copolymers prepared from POSS molecules (**Section 1.5**) have been produced and it has been suggested that they may be used in applications including molecular sieving, catalyst support and electronics.

Numerous other applications have been devised for POSS molecules. It has been suggested that if POSS can be prepared with several different functional group types attached to each individual molecule, it may be possible to create materials with delineated properties. To this end, efforts have been made to develop POSS bearing groups capable of binding catalysts, adhesion, light sensitisation and other diverse functions.[67] Due to their well defined geometry and the viability of octa-amine and octa-alcohol POSS, it has been suggested that POSS could be used as scaffolds for peptide synthesis.[76] The POSS would act as templates allowing up to eight functional groups of biological interest to be presented for study or manipulation in discrete units. Incorporating POSS into photoresists for printed circuit boards can enhance the performance of these materials through improving contrast without compromising sensitivity.[33] Silanol-functionalised POSS can bind to metal surfaces creating coatings which can reduce corrosion.[77] They can also be added to polymer coatings where they behave in a similar manner and enhance the adhesion of the mixture to metal surfaces. Semiconducting polymers could have many applications in optical devices such as electroluminescent displays and solar cells but current polymers are not very robust under what would be typical operating conditions. Incorporating POSS into these

materials offers the potential for greater levels of stability with minimal or no compromise in device performance.[78]

Due to their cubic nature and highly functionalised form, it has been proposed that POSS cubes would lend themselves to use as molecular building blocks for the preparation of extended networks. This application of POSS had only been suggested when this project was initiated,[79] but, subsequently, extended networks of alcohol functionalised POSS have been prepared indicating that the technique is viable,[31] but due to the nature of the POSS employed, the network is not robust. It was the intent of this project to develop this concept further as cubic POSS have several features that may lead them to make ideal molecular building blocks. They are robust molecules, their functional groups provide a means to link them together and their geometry is ideally suited to the preparation of porous structures.

1.5 Extended POSS Networks

One of the principle reasons for selecting octameric POSS for use as molecular building blocks for the preparation of porous materials is their effectively cubic form. POSS cubes bear functional groups at their corners and if these groups are used to link the POSS together, networks of corner linked cubes will be formed. Due to the geometry of corner linked cubes, this would result in a porous structure (***Figure 1.7***). Additional support is given to this concept when the striking resemblance between these molecules and the double four ring SBUs found in zeolitic materials is

taken into account, suggesting that POSS are well suited to the preparation of well ordered materials.

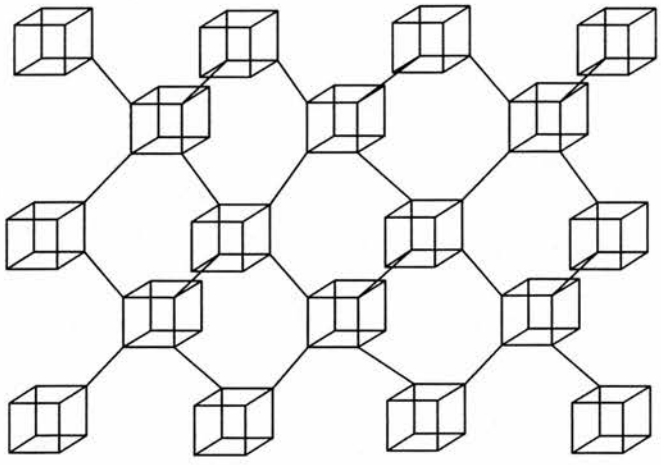

Figure 1.7. *A schematic of corner linked cubes. This structure can extend in three dimensions, but only one "layer" is shown here for clarity.*

As the functional groups will be the key structural components of the pores that are formed, varying the nature of the functional groups is likely to vary the size and shape of the pores. For example longer functional group lengths would be expected to introduce longer distances between the POSS cores in any network, resulting in larger pore diameters. The large and varied number of functionalised POSS that are currently available suggests that preparing POSS with different functional groups to form different structures should be a relatively straight forward matter. This could mean that a system developed to manage the assembly of POSS building blocks into porous networks could be applied to a range of molecules with functional groups tailored to make specific types of material.

Extended POSS Networks

The main aim of this project was to prepare porous materials with well ordered structures on a par with existing molecular sieve structures. Bringing together building units to create such structures requires a great deal of control to ensure that the desired order can be obtained.[7] In the case of the building blocks used in this project, bringing the octa-functionalised molecules into the correct orientation and ensuring that all eight groups are linked in the correct manner to neighbouring POSS also functionalised with eight groups is expected to be very difficult. It is therefore anticipated that this can only realistically be achieved through self assembly of the networks which will necessitate the preparation of POSS bearing functional groups that will allow this approach to be employed.

Functional group selection depends on the networking mechanism that will be employed to create the porous material but the mechanism will have to be of a reversible nature. By employing a reversible linking mechanism such as metal co-ordination or hydrogen bonding, the forming structure is not fixed but can be directed towards the ordered configuration that is desired. The principle guiding influence for these materials as they form will be thermodynamic stability which offers distinct advantages over the kinetically driven synthesis techniques used to prepare existing molecular sieves.

Due to the structure and geometry of the building blocks that were selected for this project, it is anticipated that the lowest energy form of these units when linked will be a well ordered porous structure. If components of the structure are out of

alignment, then they will be in a more thermodynamically unfavourable position than those which are correctly aligned and will move towards a lower energy state if the conditions during assembly allow.

Although POSS may be functionalised with moieties that have components capable of being linked together, these components must be in the correct position or orientation to allow linking to be achieved. For example, it would be expected that a conceptual POSS functionalised with pyridine groups could be linked to similar POSS through metal co-ordination if the pyridine group was the 4-isomer but linkage would be difficult if it was the 2-isomer. It was therefore considered prudent to aim to prepare POSS with functional groups that had available conformations suitable for linking of the molecules. In practice this involved attempting to prepare POSS with the linking groups at or near the outermost tip of the moieties bound to the cube.

As the intent of this project was to produce porous materials with well-defined structures, it was anticipated that POSS bearing functional groups with a degree of rigidity would be required. It was thought that flexible functional groups could fold and deform when in the structure of an extended network resulting in a material with properties that are not precisely defined. Flexible groups could also result in the collapse of porous structures, particularly when any solvents used in the assembly of these materials are removed.[7] It was therefore considered desirable to prepare POSS building blocks bearing groups that contained rigid components such as multiple bonds or aromatic systems.

In addition to rigid components, it was anticipated that sterically demanding groups would assist in the preparation of materials with well defined structures. For example, flexible components in the functional groups attached to the POSS core such as ethyl linkages could be accompanied by units such as dimethyl groups to reduce the range of movement. It was also anticipated that such groups could be used to help align the POSS networks as they formed and reduce the likelihood of interpenetration of the structure.

Proposed Systems

The most important component of the proposed POSS building blocks are considered to be the groups that will be employed to link them together. As well as providing the physical means to connect the POSS these groups must also facilitate the assembly of the material. Although numerous methods could be used to link POSS building blocks together, two were identified as appearing to be well suited to the preparation of the proposed materials.

Carboxylic acid groups were identified as key functionalities which could be incorporated into POSS molecules and used to link them together. These groups make ideal components for hydrogen bonded networks as they are effectively bi-dentate and can bind with each other (***Figure 1.8***). Although some hydrogen bonding systems only allow weak interactions between their components strong bonding can be exhibited by carboxylic acids which was expected to allow them to be used to produce relatively robust networks.[21] As hydrogen bonding is a reversible linking mechanism,

the use of carboxylic acid units was anticipated to allow for self-assembly resulting in the preparation of well ordered materials.

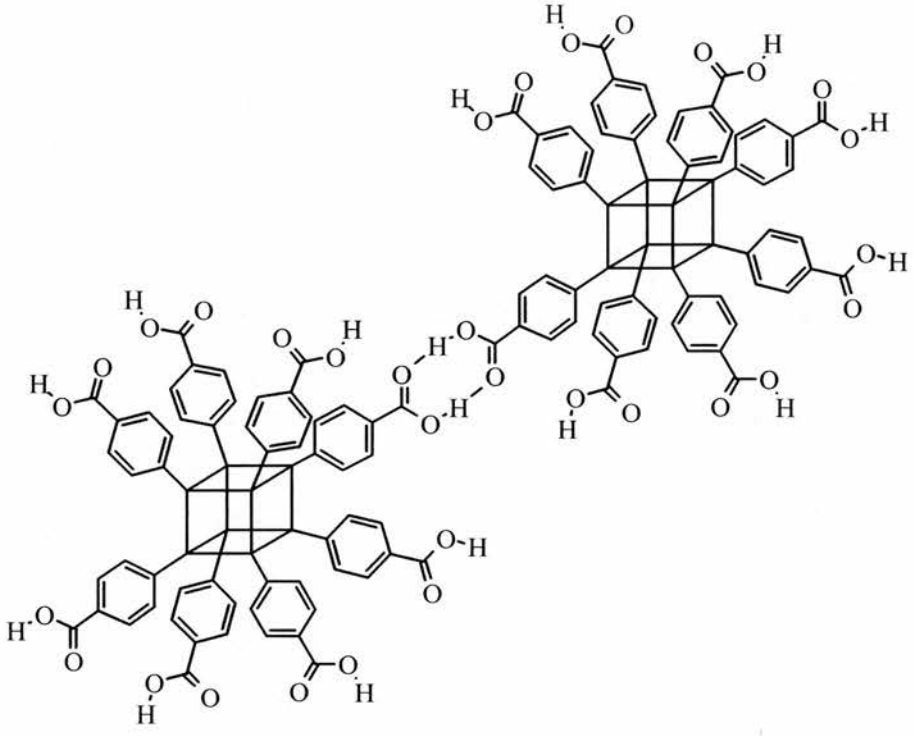

Figure 1.8. *Hydrogen bonded carboxylic acid-functionalised POSS.*

In addition to hydrogen bonding, carboxylic acid-functionalised POSS could also be linked through metal co-ordination. An excellent example of the application of metal co-ordination are the studies performed by Yaghi *et al* who have succeeded in preparing three dimensional porous strcutures from benzene tricarboxylic acid with zinc (II) forming bridging links between the acid groups (***Figure 1.9***).[29] This technique can be performed under very mild conditions or under elevated temperatures and pressures to produce relatively robust networks which have enhanced thermal stability because of the incorporation of the metal species.

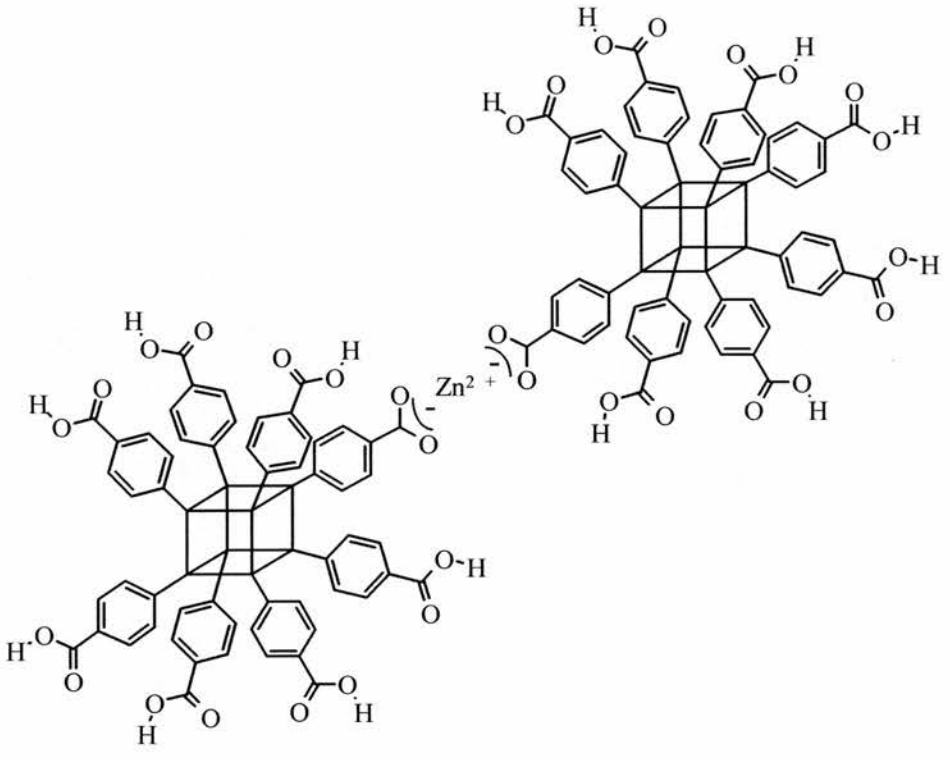

Figure 1.9. *Deprotonated carboxylic acid-functionalised POSS linked through zinc (II).*

Pyridine groups are effective ligands for co-ordination with transition metals such as silver(I) (***Figure 1.10***) and the co-ordination chemistry of this type of system has been well documented.[27, 80, 81] Several examples of complex structures assembled through metal co-ordination of pyridine groups have been reported, leading to the conclusion that this approach may also be applicable to POSS systems. As well as making excellent ligand species, pyridines have the added benefit of containing a six membered aromatic ring giving the functionality a degree of rigidity. Pyridines are also relatively easy to manipulate synthetically and capable of undergoing a range of metallation chemistry.

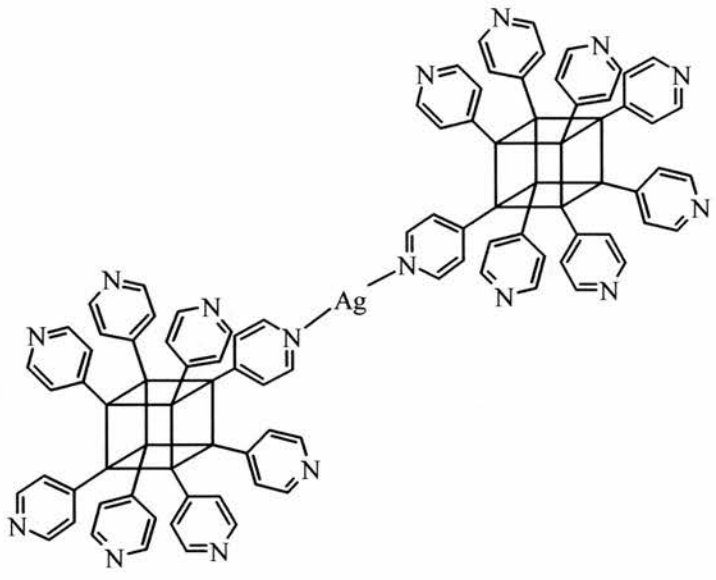

Figure 1.10. *Schematic of pyridine-functionalised POSS cubes linked through metal co-ordination.*

Although pyridine and carboxylic acid functionalised POSS were identified as having the potential to make excellent molecular building blocks, others such as isonitrile bearing POSS may also be effective.[30] It was not considered to be viable to explore the preparation of a wide range of specific functionalised POSS during this project and this led to the decision to concentrate on the preparation of carboxylic acid and pyridine bearing POSS but to also investigate different synthetic techniques which could be used to prepare functionalised POSS. By exploring the application of different synthetic techniques, this would assist in the development of the pyridine and carboxylic acid-functionalised POSS but could also lead to the preparation of new POSS which could be readily converted into a form more suitable for self assembly.

Self-Assembling POSS Networks

As has been discussed above, the intent of this project was to prepare molecular building blocks which could be linked together through hydrogen bonding and/or metal co-ordination in self-assembling processes. By virtue of the nature of these systems it was expected that they would overcome many of the problems associated with existing microporous materials and their formation.

The key POSS types that were to be developed were pyridine and carboxylic acid functionalised molecules that would lend themselves to linking through metal co-ordination and, in the case of carboxylic acid bearing POSS, hydrogen bonding. These linking mechanisms are both non-covalent and therefore lend themselves to the preparation of well ordered, self assembled networks.

For carboxylic acid-functionalised POSS, it was anticipated that the first efforts to prepare networked materials would involve attempts to use hydrogen bonding. This would provide a simple means by which these POSS could be linked and could be achieved in a number of ways. It was thought that simple crystal engineering techniques such as slow evaporation of solvents could be applicable but in the event that these were unsatisfactory, solvothermal techniques could be applied. It was thought that metal co-ordination may also be applicable for carboxylic acid bearing POSS, particularly the zinc (II) linking techniques described by Yaghi *et al.*[29]

Pyridine-functionalised POSS would not be suitable for linking through hydrogen bonding although π–π interactions between their ring systems may occur.

However, metal co-ordination was anticipated to be ideally suited to the linking of these building blocks to form extended networks. Different metal species could be used, but examples of silver (I) co-ordination have been well documented and it was anticipated that this metal would be used in initial co-ordination experiments. The assembly of complex structures from pyridine-based building blocks is achievable under mild conditions at room temperature but should this not be possible with POSS-based systems, alternative techniques such as solvothermal ripening may be applicable.

The key to preparing materials tailored to meet targeted applications is anticipated to be control of the functional groups attached to the building blocks used to prepare that material. Although the principle functionalities that were to be investigated in the project were to contain carboxylic acid and pyridine derivatives, it was thought that this would not restrict the range of units that could be placed between the POSS core and the linking group. For example, if a system was devised that could link pyridine-bearing POSS together in a controlled manner, it may, conceptually, be possible to apply this system to POSS with pyridine groups bound directly to the silicon oxygen network and POSS with a spacer group between the silicon oxygen network and the pyridine group. This could then result in two materials prepared using the same approach but with different properties because of the differences in the building blocks used.

Advantages over Existing Systems

If the approaches described above can be successfully employed to prepare porous materials, it is anticipated that they will provide a system for preparing such materials in a manner that offers benefits over established technologies.

By using a modular approach to the preparation of porous materials, the "one pot" approach generally encountered in molecular sieve preparation is no longer required. The use of building blocks will be a thermodynamically driven process which will be easier to understand and control than the mechanisms operating during the hydrothermal techniques generally employed in the preparation of molecular sieves. It is anticipated that the key to controlling the properties of the materials prepared will be the preparation of the POSS building blocks. The POSS will determine the nature of the material produced which will place the onus on the understanding of the chemistry required to synthesise suitable POSS rather than the kinetics encountered in a hydrothermal reaction.

Modular materials prepared in the manner proposed here are typically crystalline in nature or at least have well-ordered structures. This is expected to mean that materials prepared from POSS building blocks will have well defined structures with much more tightly controlled pore sizes and shapes than silicas, inorganic/organic hybrids or copolymerised POSS systems. In addition, a well-ordered POSS network will contain only very small numbers of unlinked functional groups. This would result in materials which lack free functionalities such as hydroxyl

groups found in sol-gel materials, thereby reducing the possibilities for reaction or interaction between the fabric of the solid and materials within it.

1.6 POSS Copolymers

Although the main aim of this project was to develop a route to the rational preparation of well-ordered porous materials from molecular building blocks, hydrosilylatively copolymerised POSS systems with little order in their structures were also investigated as part of this study.

Experiments investigating the linking of POSS through hydrosilylation were first reported by Agaskar in 1989.[82] A bifunctional unit was hydrosilylated between T10 POSS to yield an amorphous polymeric material which although not microporous could absorb quantities of THF. As it was expected that the geometry of the POSS would induce a high level of porosity within the material, it was assumed that structural interpenetration was occurring.

In 1990, Hoebbel *et al* reported the copolymerisation of T8 POSS without the use of a non-POSS linking unit.[83] It was found that hydrosilylation of appropriately functionalised POSS in 1:1 ratios using platinum divinyltetramethyldisiloxane resulted in the formation of insoluble polymers. Despite the geometric constraints associated with connecting cubic structures together through their corners, the materials produced had low surface areas of 1 to 8 $m^2 g^{-1}$. Subsequent studies performed by Hoebbel and co-workers produced copolymers with higher surface

areas of up to 360 $m^2 g^{-1}$ using POSS with relatively long functional groups which led them to the conclusion that only inter-POSS linkages of six atoms or longer would produce porous copolymers.[84]

Harrison and Kannengieser then paired appropriately functionalised T6 and T8 POSS, linking them together through hydrosilylation and hydrolysis reactions to yield porous copolymers.[75] Although these materials had inter-POSS linkages less than 6 atoms in length, their porosity exceeded that of the materials prepared in the earlier experiments, contradicting the conclusions made by Hoebbel *et al.*

The viability of preparing copolymers from POSS and spherosilicates with short and long linkages between the cages was confirmed by Zhang *et al* who produced a range of porous copolymers and performed a systematic study of these materials.[6] As their findings contradicted the results obtained from the Hoebbel studies, they concluded that the porosity of this type of material is dependent on the experimental methodology and conditions as well as the reactants used.

Copolymerised POSS form as gels and take on a glassy appearance when dried. Once dried, these materials are physically robust and are typically stable up to 400 °C. The surface areas of the reported copolymers vary enormously with some being effectively non-porous while others have surface areas of nearly 900 $m^2 g^{-1}$. When consistent methodologies are used, as in the study performed by Zhang *et al*, a degree of correlation can be observed between porosity and the length of the functional groups attached to the POSS precursors. One may expect the use of longer functional groups to result in materials with higher surface areas as the longer groups

would be expected to create larger pores, but the opposite is actually observed.[6] It has been assumed that the cause of this effect is the higher level of geometric constraint associated with covalently linking POSS with short functional groups together than there is when POSS with longer groups are linked. Longer functional groups can also allow bending or folding of the inter-POSS links and structural interpenetration, resulting in denser materials with lower surface areas.

Although the high surface areas of porous copolymers may allow them to find many applications, the properties of these materials are not well enough defined to allow them to be used in applications where precise molecular recognition is required. This type of material can give access to micropores, but there is a distribution of pore sizes across the micropore range and mesopores can also be present in these materials. As these materials are still at an early stage of development, it is conceivable that techniques may be developed to control the range of pore sizes and architecture within them. They may, however, find applications in heterogeneous catalysis at their current stage of development but this is likely to be restricted to reactions where the geometry of the reaction environment does not have to be tightly controlled.

In most instances, it has been found that the steric constraints imposed on the copolymers, both porous and non-porous, as they were formed lead to a considerable number of the functional groups being unable to react. As for the surface areas of these materials, the degree of cross linking is dependent on the nature of the POSS precursors. In some cases, cross linking can result in essentially all of the functional groups reacting, but in others, reaction only goes to approximately 80% completion.

The findings of previous studies have come to conflicting conclusions and copolymers with different properties have been prepared from very similar if not identical starting materials. This indicates that the character of this type of material depends largely on the reaction conditions employed to prepare it as per Zhang's conclusions. However, the studies which have successfully prepared porous copolymers all produced materials which contain a range of pore sizes and lack order in their structure. Harrison and Kannengieser suggested that the copolymers they prepared are completely amorphous in form but Zhang *et al* have suggested that there is an underlying structure to their copolymers although it may be very poorly defined. Based on observations made during their study, Zhang *et al* also suggest that the formation of the POSS aggregates as the polymers form almost becomes a self-assembly process with POSS joining the growing structure in a 'zipping' manner.

Although the majority of silsesquioxane copolymers have been prepared by POSS-POSS reactions, the possibility of preparing copolymers by hydrosilylating cubic POSS with linking/spacer units has also been investigated. As has already been discussed, Agaskar used linking units to assemble a copolymer from a T10 POSS. Schultze *et al* performed a comparative study by preparing four different copolymers, one using a pair of POSS, the others POSS and linking/spacer molecules.[85] Three spacer types were used to allow reaction between di-functional, tri-functional and tetra-functional units. While the POSS-POSS copolymer was found to have a high surface area, the others all had very low surface areas but all three spacer units were flexible and lacked the steric bulk of the POSS. This may have allowed structural interpenetration or folding and compression of the copolymer structure, resulting in the low surface areas.

The study of copolymerised POSS is still a relatively new field, but these materials may offer several advantages over current molecular sieves and inorganic/organic hybrids in certain applications.

Although they typically contain unreacted groups, these are not the hydroxyl groups which are typically found in the products of sol-gel reactions which means that these materials are not hydrophilic in nature. As these materials contain rigid components in the form of the silicon-oxygen cores of the POSS, they are likely to require less onerous drying than the products of sol-gel reactions to maintain high surface areas as they will, to a certain extent, be self supporting. An additional advantage over sol-gel reactions are the rapid reaction times observed for hydrosilylative copolymerisation which can be as little as 20 minutes.

Attempting to tailor POSS-based copolymers towards meeting specific applications is likely to be much easier than tailoring current inorganic oxide molecular sieves. As the copolymers are prepared from pre-formed components and the integrity of these components is unaffected by the copolymerisation process, the nature of the resultant material is affected by the nature of these components.

By studying the preparation of this type of material, the effect that the precursors have on the nature of the copolymer and the conditions required to produce porous materials, it was hoped that the information that would be gained could be applied to the preparation of more ordered systems. In addition to providing information on the mechanics of assembling porous networks, preparing

copolymerised POSS would provide materials which could be used to investigate the viability of preparing catalytic materials from POSS immobilised in a porous array. Copolymers are ideal for preliminary studies of this type as the links between the POSS are all covalent and disruption of hydrogen-bonded networks or co-ordinated metals is not an issue.

1.7 Catalysts from POSS Networks/Copolymers

Porous POSS networks and copolymers are likely to find applications as molecular sieves/selective membranes[17] and as dielectric materials[21] but they should also lend themselves to use in catalysis either as catalysts in their own right or as catalyst supports. The goal of this project was not only to develop a system capable of preparing well-defined microporous materials but to enable that system to also be used to prepare catalytically active microporous materials. POSS-based systems lend themselves to the preparation of catalytic materials and it was anticipated that this could be achieved in a number of ways.

Uncombined Functional Groups

The unreacted functional groups found in POSS copolymers, could be accessed through the pore structures of these materials and be utilised to form catalyst supports. By reacting these groups with substrates such as phosphines,[86] structures capable of retaining catalytically active species such as transition metals could be introduced into the material. The principle drawbacks of this technique are that the

catalytic species and/or support must be introduced throughout a pre-formed structure and the pore diameter at the catalytic site must be large enough to accommodate both the reactants and the catalytic component.

Using unreacted functional groups to prepare catalyst supports may not be applicable to well-ordered POSS networks as, by their very definition, there will be very few uncombined groups present in these materials. It is conceivable however, that POSS bearing a small number of functional groups that will not form links with other POSS could be used during the preparation of extended networks to introduce free functional groups. If the number of these groups was controlled, it may be possible to produce a well-ordered structure containing "flaws" with each "flaw" having the potential to be converted into a catalytic site.

Incorporated Transition Metals

The incorporation of transition metal species within the fabric of POSS networks and copolymers is likely to form the mainstay of attempts to prepare active catalysts from porous POSS-based materials. Fixing transition metals within porous materials could generate catalytic systems suitable for use on a wide variety of industrially important processes such as epoxidation and olefin metathesis.[87]

Inter-POSS Links

An obvious position for the incorporation of metals within the structure of an ordered POSS network formed through co-ordination is in the links between the

cubes. This would result in an even distribution of the metal species throughout the whole network at well-defined locations. However, the interaction between the cubes' functional groups and the metal could render any potential catalytic activity ineffective. It is also conceivable that the catalytic cycle associated with the metal species could disrupt the structural integrity of the networked solid as the reactants interact with the metal.[29]

Metal Containing POSS

Although the approaches listed above may allow the preparation of catalytically active porous solids, it is more likely that transition metals such as titanium and vanadium will be incorporated into the POSS themselves. This has already been achieved in discrete POSS through a variety of routes to produce catalytically active species.

Partial cage silsesquioxanes have been capped with titanium (***Figure 1.11***),[88] vanadium,[89, 90] molybdenum,[91] and zirconium[92] species leading to monomeric and dimeric molecules. The catalytic potential of these metal bearing systems is mixed, with some proving to be effective catalysts for oxidation and epoxidation reactions while others are essentially inert. These systems are usually prepared from partial cubes hydrolytically condensed from silanes bearing cyclopentyl, cyclohexyl or cycloheptyl groups with a tri-functional metal species being added to finish the open corner.

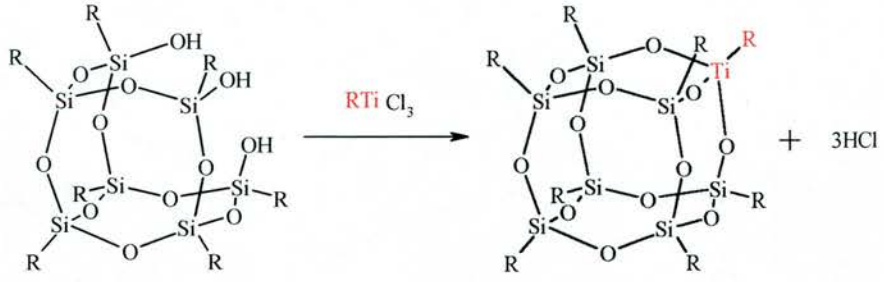

Figure 1.11. *Corner capping of partial POSS cube.*

As the cube structure is incomplete until the metal species has been introduced, the catalytic component of the final POSS network may have to be emplaced before the network is assembled. This may cause problems during the preparation of the network as the metal could be susceptible to side reactions or the moiety associated with the metal could act in an unfavourable manner during the assembly process. However, as the catalytic site would be part of the precursors, this approach could lead to well-distributed, well-defined catalytic sites in the final network. An additional problem with this type of system is that no corner-capped POSS have yet been prepared with functional groups that lend themselves to the preparation of extended networks of POSS. This means that to apply this approach to preparing catalytic porous solids, new corner-capped species will have to be prepared either through the identification of suitable hydrolysable silanes or through manipulation of the functionalities associated with existing corner-capped POSS.

Another route to incorporate metals into POSS cubes is to introduce them while the cube is being formed. Hydrolytic condensation of a metal triol with a silicon triol can produce cubes with alternating corners of silicon and metal (***Figure 1.12***).[93]

Here, condensation occurs as for pure silanol precursors but the presence of a second species produces a mixed structure.

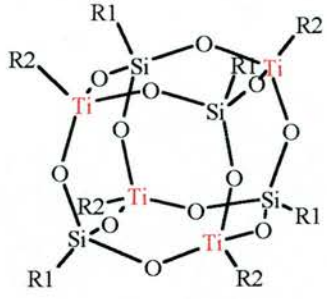

Figure 1.12. *A mixed silicon/titanium cube.*

Again, the application of this approach will be affected to a great extent by the type of non-hydrolysable groups bound to the metal and the silicon. These determine how the POSS will form and also how it can be incorporated into an extended structure. It may be the case that the groups required to allow mixed POSS formation will be incompatible with porous network assembly and require extensive synthetic manipulation. As with the corner-capped POSS, the catalytic properties of these molecules are likely to vary from highly efficient to essentially inactive, depending on the type of metal used and functional groups attached to both the silicon and metal species.

Recently it has been demonstrated by Feher *et al* that it is possible to modify the structure of POSS after the molecule has been assembled. Strong acids and bases can be used to break open the edges and/or corners of POSS cubes allowing the insertion of metals or heteroatoms (***Figure 1.13***).[94, 95, 96] This technique has been successfully applied to monomeric POSS but it may also be possible to use it with copolymers and networks allowing the emplacement of metal species after a porous

structure has been formed. Care must be taken however to ensure that the functional groups attached to the POSS cores are not susceptible to the cleavage process and that the reaction is not allowed to go too far resulting in destruction of the molecule.[97] The cleavage technique has only been reported as being effective on cyclopentyl, cyclohexyl and cycloheptyl silsesquioxanes but procedures are currently being developed by Feher and co-workers for the cleavage of cubes bearing more useful functional groups.[98]

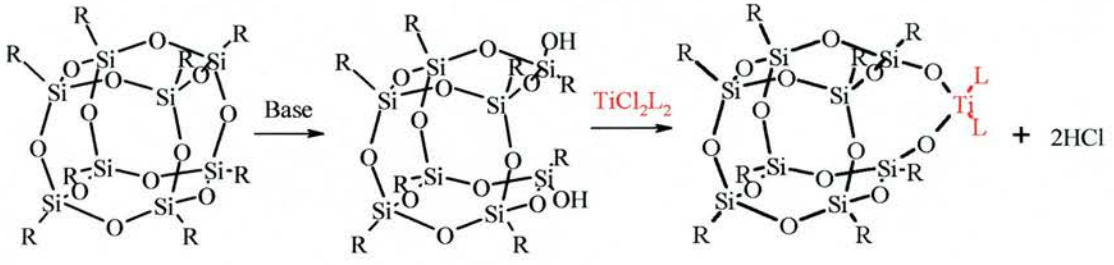

Figure 1.13. *An example of alkaline silsesquioxane cleavage followed by titanium insertion.*

Any catalytic properties these metal-containing POSS possess as discrete molecules may be also be present when they are incorporated into copolymers and extended networks. This should allow the assembling of porous solids which have catalytic sites at well-defined positions in their structures. Due to the multiple forms that acid and base cleavage can produce, precise control of the position of the catalytic site introduced through the cleavage may not be possible however.

It is conceivable that acid/base cleavage could have two roles to play in the preparation of catalytically active POSS-based structures. This method allows discrete POSS to be manipulated and metal species introduced to their structures prior to any

self-assembly or copolymerisation process. This approach would be appropriate for POSS that are to be self-assembled *via* a linkage mechanism which would be incompatible with acid or base cleavage.

As discussed earlier, the introduction of the catalytic component to the POSS prior to preparation of the network or copolymer may cause problems during the assembly process. An alternative approach would be to apply the POSS cleavage technique to pre-assembled networks or copolymers if it can be induced to operate in the correct manner within the material. This would allow the POSS to be combined in a fashion that best suits the preparation of the porous material with the formation of the catalyst being undertaken once the network or copolymer has been formed.

Selectivity

One of the most useful features of inorganic oxide molecular sieve-based catalysts is their molecular-recognition abilities.[1] Due to the tightly controlled structures of these materials, they are able to perform molecular recognition with resolutions in the region of angstroms. This can be used to prevent unwanted reactants entering the material and/or control the reaction and the types of product formed. This can give them very specific catalytic properties and it was hoped that the molecular building block approach taken in this project could result in materials with similar selectivity. Specific molecular recognition will only be achieved if the structures of the material can be precisely defined which means that POSS copolymers are unlikely to be of use in this type of application.

Preparation of Catalysts

Although any of the techniques described above may find application in the modular materials that this project was attempting to deliver, it was anticipated that POSS cleavage would probably be the most useful approach. Although the routes using corner capping or mixed condensations were appealing, the development of suitable precursors or the synthetic manipulation of the existing corner capping systems was expected to be difficult and time consuming. The manipulation of uncombined functional groups was also appealing, but this was to be studied by another student within our research group and was therefore not considered in this project.

By virtue of the fact that POSS cleavage could, potentially, be employed on both discrete and networked POSS, it was selected as the initial technique which would be used in efforts to prepare catalytically active POSS-based materials. It was therefore proposed that attempts would be made to introduce metal species into discrete POSS building blocks once they had been developed and a means to network them had been established. Efforts would then be made to use cube cleavage on networked POSS to determine which may be the best approach to employ.

This study was dependent on the preparation of suitable building blocks and their assembly into networks which was expected to take a considerable time to achieve. To provide early information on the cleavage of assembled POSS, it was proposed that POSS-based copolymers would be used as a test bed for this reaction. As well as indicating that the technique was viable and that the strategy of this project

was not flawed, such experiments also had the potential to lead to new, potentially useful catalytic materials.

1.8 Project Aims and Objectives

The overarching aim of this project was to progress towards the preparation of microporous catalysts assembled from molecular building blocks, providing an alternative to existing technologies. It was recognised that that this may not be fully realisable during the timeframe of this project and the work was therefore broken down into several key areas:

- Investigation of techniques applicable to the preparation functionalised POSS
- Preparation of molecular building blocks suitable for self-assembly
- Preparation of extended POSS networks
- Investigation of porous POSS copolymer preparation
- Investigation of the potential for POSS-based solids to be used to form catalytic materials

Molecular Building Blocks

One of the main goals for this project was the preparation of molecular building blocks from POSS to allow the preparation of porous modular materials. To this end, attempts were made to prepare carboxylic acid-functionalised POSS, pyridine-functionalised POSS and to explore synthetic pathways that could produce other potentially useful functionalised POSS.

Extended POSS Networks

In the event that suitable molecular building blocks could be prepared, it was intended that efforts would be made to prepare extended networks from these materials. Initially, simple methods such as hydrogen bonding or room temperature metal co-ordination would be used, with techniques such as solvothermal ripening being employed if these were unsuccessful.

Copolymers

In parallel to investigation of the preparation of molecular building blocks and their assembly into extended networks, the copolymerisation of vinyl and silicon hydride-functionalised POSS to produce porous materials was investigated. As it had already been demonstrated that porous materials could be produced through the copolymerisation of POSS cubes, these experiments had two objectives; firstly, the investigation of links between the POSS functional groups and copolymer porosity and secondly, the creation of materials suitable for preliminary studies into the preparation of catalysts from interlinked POSS.

Catalysts

If rapid progress was made in the preparation of appropriate molecular building blocks followed by their assembly into porous extended networks, it was intended that the potential for the preparation of catalytic materials from these networks would be investigated. The principle approaches that would be taken in an

effort to produce catalytic materials would be those of incorporation of transition metals in the POSS building blocks and the cleavage of networked POSS to allow transition metals to be incorporated into their structures.

It was recognised that the development of molecular building blocks from POSS and the subsequent creation of porous solids from them was likely to be a lengthy process, so in parallel to this work, attempts were made to apply acid cleavage to POSS copolymers. This would have impacts on the development of extended network solids as it would indicate if it would be possible to incorporate metal species into porous materials after they had been formed of if the catalytic sites would have to be introduced while the material was forming.

Secondary Goals

In the course of this work, it was expected that new materials would be prepared which would not necessarily fulfil the main goals of this project. For example, new POSS could be prepared which may not be suitable for self-assembly or copolymerisation but may find applications elsewhere. It was therefore intended that if such materials were produced, these would be documented to a level which could allow other researchers to develop them further for other applications.

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Chapter 2 Carboxylic Acid-Functionalised POSS

2.1 General Introduction

The potential utility of carboxylic acid-functionalised POSS in the formation of extended networks made the preparation of this type of molecule one of the main goals of this project. Prior to this study, no descriptions of aldehyde or carboxylic acid-functionalised POSS were available but the synthesis of alcohol and ester-bearing POSS had been reported.[1, 2, 3] Carboxylic acid groups by their very nature are susceptible to reaction and this, combined with the synthetic demands of silsesquioxane chemistry, complicates the preparation of POSS bearing these groups. To find an applicable preparative technique to produce this type of molecule, four different approaches were taken in this study.

A cobalt-based catalyst system has been used by Ishii *et al* to oxidise alkylbenzenes to carboxylic acids[4] and it was thought that this system could be applied to suitably functionalised POSS. Hydrolytic condensation of 4-tolyltrichlorosilane can be used to produce a POSS cube bearing tolyl groups[5] which appeared ideally suited to this type of oxidation reaction and experiments were performed to investigate the performance of the catalyst system on this molecule.

The direct hydrosilylation of carboxylic acid derivatives to POSS cores was appealing, but this approach was ruled out due to side reactions between the acid and silicon hydride groups that would also be catalysed during the process.[6] Protection of carboxylic acids by esterification prevents side reactions promoted by hydrosilylation

catalysts, allowing them to be involved in hydrosilylation reactions when in this protected form. Feher and co-workers employed hydrosilylation to prepare an ester-functionalised POSS[3] which was used in this project as the starting material in a series of experiments investigating the possibility of producing carboxylic acid functionalised cubes through hydrolysis of their ester equivalents.

Oxidation of alcohol and aldehyde groups is a method frequently used to prepare carboxylic acids[7,8] and can be accomplished through a variety of synthetic techniques. Although several alcohol-functionalised POSS have been documented,[1, 2] aldehyde groups can be oxidised under milder conditions that are more likely to leave a POSS core intact. New benzaldehyde functionalised POSS were therefore prepared through the hydrosilylation of bromobenzaldehyde derivatives to an octavinyl silsesquioxane[9, 10] and attempts were then made to oxidise these molecules.

Trichlorosilanes and triethoxysilanes that can be hydrolytically condensed to produce POSS with moieties suitable for conversion to carboxylic acid groups have not yet been reported. The techniques employed to synthesise the benzaldehyde-bearing POSS described above offered the possibility of preparing trifunctional silanes suitable for the hydrolytic condensation of POSS with rigid moieties terminating in aldehyde groups. The oxidation of such POSS could produce potentially useful molecular building blocks and attempts have therefore been made to prepare appropriate silane precursors.

These experiments were undertaken over a lengthy period of time and success was only encountered towards the end of the project. Although carboxylic acid

functionalised POSS were prepared, there was insufficient time to allow an investigation into the networking of these molecules to be made.

2.2 Tolyl Group Oxidation

Introduction

A catalyst system using cobalt acetylacetonate, $Co(acac)_2$ or $Co(acac)_3$, and N-hydroxyphthalimide has been shown to be capable of oxidising cycloalkanes and alkylbenzenes under very mild conditions.[4, 11] Cycloalkanes undergo oxidation at their ring carbons while the alkyl groups of alkyl benzenes are converted to alcohols or carboxylic acids depending on the precursor. The mechanism of the reaction is not yet fully understood but high yields have been obtained and toluene has been oxidised to benzoic acid with 92% conversion.

This system appears ideal for use with POSS and experiments were conducted using 1,3,5,7,9,11,13,15-octakis(4-tolyl)pentacyclo[9.5.1.$1^{3,9}$.$1^{5,15}$.$1^{7,13}$]octasiloxane $[SiO_{3/2}C_7H_7]_8$ (**1**), a *p*-tolyl-functionalised POSS (***Figure 2.1***).[5] By using a POSS with an aromatic ring attached directly to the silsesquioxane core it was expected that a rigid building block would be formed which would be ideal for the preparation of well ordered solids.

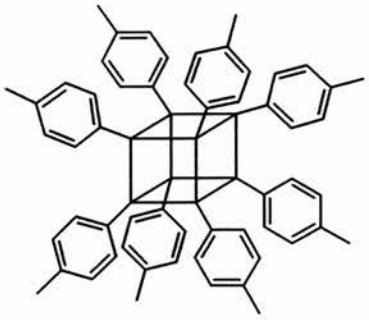


Figure 2.1. *4-Tolyl-functionalised POSS (1).*

Results and Discussion

POSS **1** was prepared in only 5.0% yield but a high yield was not crucial to the course of these experiments. Simply filtering off the product from the hydrolytic condensation solution gave material that was ready for use without further purification.

Attempts to oxidise **1** were made using $Co(acac)_2$ under a range of conditions, but no oxidation of tolyl groups was observed in any of the reactions indicating that the catalyst system is not effective with this particular POSS. It has been reported that the silicon oxygen network of POSS can exert a strong electron withdrawing effect through aromatic ring systems[1] and this may be acting on the methyl groups to deactivate them towards the catalyst, resulting in the absence of reaction. Without determining a mechanism for the operation of the catalyst system it is impossible to say if this is actually the case but due to the relative simplicity of the POSS molecule, this appears to be the most likely explanation.

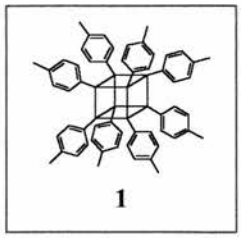
Conclusions

It appears that $Co(acac)_2$ catalysed oxidation of **1** is not possible but it is known that this particular catalyst system can oxidise tolyl groups effectively. If the electron withdrawing effect of the POSS core is responsible for this lack of activity, it may be possible to use this oxidation technique on tolyl-functionalised POSS where there are several atoms between the aromatic ring and the core. The preparation and oxidation of such molecules was not attempted as the synthesis of benzaldehyde functionalised POSS with similar conformations was being investigated and offered a simple route to carboxylic acid functionalised POSS (**Section 2.4**).

Experimental

General Experimental. Acetone (Cannon Chemicals), *p*-trichlorotolylsilane (Aldrich), acetic acid (Fisons), N-hydroxyphthalimide (Aldrich), magnesium sulphate (Fisher), diethyl ether (BDH) and oxygen (BOC) were all used as supplied. $Co(acac)_2$ was kindly donated by Dr. Gary Hix and was used as supplied. Information on the analytical equipment and techniques is provided in **Appendix B**.

Preparation of $[SiO_{3/2}C_6H_4CH_3]_8$ (1). *p*-Trichlorotolylsilane (2.82 g, 12.5 mmol) was slowly added to an ice cooled acetone/water solution (80% v/v) and the resultant mixture was refluxed for 3 days. On cooling, the solution was allowed to stand for 2 days to allow the product to precipitate out of solution. Filtration was then used to recover the product which was dried to give a white powder which analysis



1

confirmed as $[SiO_{3/2}C_6H_4CH_3]_8$ (**1**) (0.09 g, 5 %).[5] ^{1}H NMR ($CDCl_3$) δ 7.66 (d, J_{HH} = 7.9 Hz, C**H**, 2H), 7.18 (d, J_{HH} = 7.8 Hz, C**H**, 2H), 2.36 (s, C**H**$_3$, 3H). ^{13}C NMR ($CDCl_3$) δ 140.58 (**C**-CH_3), 134.29 (**C**H), 128.58 (**C**H), 127.07 (**C**-Si), 21.66 (**C**H_3). ν_{max}/cm^{-1} (KBr disk) 3064 (w, aryl CH), 3023 (w, aryl CH), 3011 (w, aryl CH), 2961 (vw), 2918 (vw), 2858 (vw), 1605 (w, aromatic ring), 1395 (vw), 1376 (w, SiC), 1193 (w), 1131 (s, SiO), 1098 (s), 1022 (w), 801 (w, aryl CH), 685 (w), 575 (m), 499 (m), 479 (m, SiO). Decomposition begins at 215 °C

Attempted oxidation of $[SiO_{3/2}C_6H_4CH_3]_8$. Acetic acid (5 cm^3) was added to a mixture of **1** (0.075 g, 0.065 mmol), N-hydroxyphthalimide (0.0085 g, 0.052 mmol) and $Co(acac)_2$ (0.0008g) under an atmosphere of oxygen. A balloon filled with oxygen was attached to the reaction vessel and the solution was heated at reflux for 10 hours. Once cooled, the reaction mixture was added to water (30 cm^3), extracted with diethyl ether (3 × 50 cm^3) and the combined organic components were dried over magnesium sulphate. The solvent was removed under reduced pressure to yield unreacted **1** (0.06 g).

This experiment was repeated with double the quantity of $Co(acac)_2$ and N-hydroxyphthalimide that was used in the first attempt before a further attempt was made with a 36 hour reaction time. No discernible oxidation of **1** was observed in either experiment.

2.3 Ester Hydrolysis

Introduction

As has been discussed earlier, direct hydrosilsylation of carboxylic acid derivatives to silsesquioxanes is not possible because hydrosilylation catalysts also promote reaction between the acid protons and any vinyl groups present.[6] Protection of carboxylic acid groups can be afforded by replacing the vulnerable acid protons with alkyl groups to form esters which are not susceptible to reactions promoted by hydrosilylation catalysts.

Esterification is regularly used in organic chemistry to protect carboxylic acids during synthetic reactions with de-protection generally being brought about by acid or base-catalysed hydrolysis.[12] Base hydrolysis is the most commonly used technique and is generally regarded as the superior route as the reaction is a non-reversible process. Acid-catalysed hydrolysis is also effective but the reaction is reversible and care must be taken to avoid reformation of the ester.

Feher *et al* demonstrated that a vinyl ester could be hydrosilylated with 1,3,5,7,9,11,13,15-octakispentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane , $[SiO_{3/2}H]_8$ (**2**),[13] in high yield to produce $[SiO_{3/2}CH_2CH_2C(CH_3)_2CH_2CO_2CH_3]_8$ (**3**) (***Figure 2.2***).[3] Hydrosilylation reactions can yield mixed products but in this case, the dimethyl group of the methyl-3,3-dimethyl-4-pentanoate directs the reaction towards the terminal carbon of the vinyl group.

During the experimental period of this study a literature review was undertaken to determine if other suitable ester-functionalised POSS had been reported but none were found. The preparation of new ester-functionalised POSS was not pursued however, as the cube developed by Feher and co-workers has a simple structure which was expected to reduce the risk of side reactions during attempts to hydrolyse it. On obtaining positive results, efforts would have been made to prepare new ester-functionalised silsesquioxanes with the aim of preparing a variety of carboxylic acid-functionalised POSS.

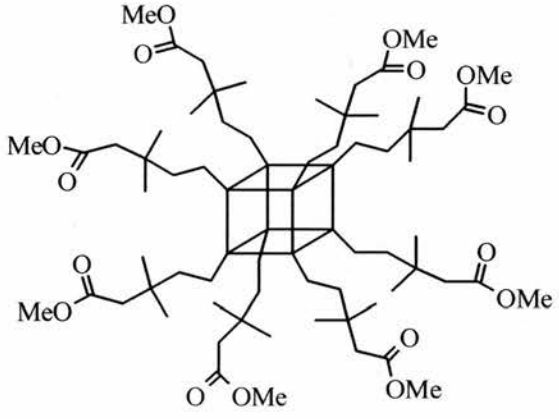


Figure 2.2. *Ester-functionalised POSS* $[SiO_{3/2}CH_2CH_2C(CH_3)_2CH_2CO_2CH_3]_8$ ***(3).***

Attempts to carry out a base-catalysed hydrolysis of **3** were expected to result in side reactions with the silsesquioxane core as well as ester group hydrolysis and this approach was not pursued. Despite the reaction being reversible, acid catalysed hydrolysis appeared to be the only recourse and three systems that had been reported as being effective were employed.

Hydrochloric acid has been successfully used in hydrolysis reactions[14, 15] and was the obvious choice for the initial attempt to perform acid hydrolysis. Sulphuric

acid has also been successfully employed in ester hydrolysis[16, 17] and was used in subsequent experiments to provide a more active alternative to hydrochloric acid. Finally, attempts were made to perform the hydrolysis reaction using a hydrolysis medium consisting of a mixture of acetic acid, sulphuric acid and methanesulphonic acid which had been reported as being mild yet effective.[18]

Results and Discussion

A slight variation on the method used by Agaskar[13] was employed to prepare **2**. A mixture of **2** and $[SiO_{3/2}H]_{10}$ was prepared in Agaskar's experiments with the $[SiO_{3/2}H]_{10}$ being removed by washing the mixture with hexane to dissolve this more soluble material. This process was found to be unsatisfactory in these experiments as a quantity of **2** was also removed reducing the recovered yield, but re-crystallisation was found to produce pure **2** in yields of up to 11.8 %. The ester-functionalised POSS, **3**, was prepared in 67.0 % yield using the method described by Feher *et al.*[3]

Refluxing **3** in 37 % hydrochloric acid was a simple approach, but reports of the successful application of this method indicate that this is an effective technique. It was therefore expected that even if a mediocre yield was obtained, a number of the ester groups would be hydrolysed to carboxylic acids. No hydrolysis was observed during a 3 hour reaction period and the experiment was repeated over 3 days to yield **4**. During this extended reaction time no detectable carboxylic acid groups were produced and cleavage of the silicon-carbon bonds linking the functional groups to the POSS core occurred. No satisfactory NMR data was obtained as the reaction product is essentially insoluble in NMR solvents, but FTIR indicates that a number of

the original ester moieties are still present in the material. Relative to the SiO absorptions, those due to the ester groups are much smaller than those observed from samples of **3**, suggesting that a large number of ester groups have been removed.

Although sulphuric acid-catalysed hydrolysis had been successful in other cases here, the addition of 95% sulphuric acid to the ester-functionalised cube resulted in the destruction of the molecule. This was not entirely surprising as it was known that strong acids can attack the carbon-silicon bonds linking the functional groups to the silicon-oxygen core and even attack the core itself.[19] Attempting the hydrolysis using 0.1M and 1.0M sulphuric acid left the structure of the molecule intact, but failed to promote hydrolysis with **3** being recovered on completion of experiments performed at room temperature and under reflux conditions.

It was anticipated that hydrolysis of the ester using the acetic acid technique would prove successful but while the starting material was consumed, the expected product was not formed. Functional group cleavage occurred rather than hydrolysis, both under reflux conditions and at room temperature resulting in the formation of an inert silsesquioxane or silica material (**6**) and, potentially, volatile components which were removed during the experimental work up.

All of these experiments were based on successful hydrolysis experiments involving esters containing methoxy groups.[14, 15, 16, 17, 18] The majority of these reactions were performed with esters which lacked a dimethyl group but had the same ester group as **3** and were successfully hydrolysed to carboxylic acids. It may therefore be possible, although unlikely, that the dimethyl group of **3** has some

influence on the outcome of the reaction although it is attached to the β carbon relative to the ester group carbon.

Hydrolysing the ester groups of **3** using the techniques employed here may be possible, but it appears that acid-promoted cleavage of the moieties from the POSS core occurs before this can be achieved. The methoxy groups are known to be poor leaving groups and it may be possible to achieve hydrolysis under milder conditions if better leaving groups can be incorporated into the original POSS molecule.

Conclusions

Hydrolysis of the ester-functionalised POSS **3** has not proved to be as simple as was first anticipated and no carboxylic acid groups were synthesised. The ester moiety has a simple composition and it was thought that this would mean that there would be little to obstruct the hydrolysis reaction. It was found however, that either no reaction occurred or the functional groups underwent cleavage from the POSS. Using POSS with different ester groups may allow the reaction to proceed as planned and further work in this area would have to centre around the preparation of new ester-functionalised POSS.

Feher *et al* chose methyl-3,3-dimethyl-4-pentenoate as the vinyl ester precursor for their experiments to increase the percentage of terminal carbon hydrosilylation but vinyl esters with a similar structure and better leaving groups can be prepared. Although not commercially available, esters such as 3,3-dimethylpent-4-enoic acid ethyl ester,[19] 4-vinylbenzoic acid propyl ester[20] and acrylic acid 2,3,4,5,6-

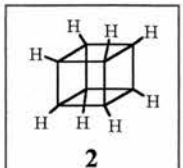
pentafluorophenyl ester[21] have been synthesised and could be used to prepare ester-functionalised POSS cubes that would be expected to have better leaving groups than **3**.

The poor results obtained in these experiments led to the postponement of further work in this area in favour of experiments into the oxidation of aldehyde functionalised POSS which were proving to be more successful (**Section 2.4**).

Experimental

General Experimental. Trichlorosilane (Aldrich), hexane (Ultrafine), tolune (Ultrafine), ferric chloride (Lancaster), methanol (Ultrafine), calcium chloride (Fisher), potassium carbonate (Fisons), chloroplatinic acid (Aldrich), sulphuric acid (Prolabo), hydrochloric acid (Fisher), glacial acetic acid (Fisons), methane sulphonic acid (Aldrich), magnesium sulphate (Fluka) and diethyl ether (BDH) were used as supplied. Hexane for hydrosilylation was dried over calcium chloride (Aldrich) and distilled from sodium (Fisons) immediately before use. Isopropanol (Fisher) was dried with calcium hydride (Aldrich) and distilled on to Linde type 4A molecular sieves (Prolabo). Information on the analytical equipment and techniques is provided in **Appendix B**.

Preparation of $[SiO_{3/2}H]_8$ (2). Trichlorosilane (20 cm^3, 0.2 mol) dissolved in hexane (150 cm^3) was added to a mixture of ferric chloride (50 g, 308 mmol), methanol (40 cm^3), conc. hydrochloric acid (20 cm^3), toluene (50 cm^3) and hexane (350 cm^3) over a period of 9 hours as per the

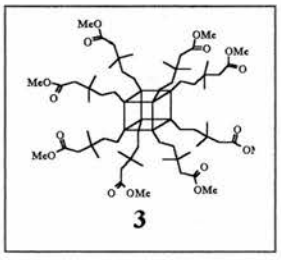


2

method described by Agaskar.[13] Although the reaction and work-up described by Agaskar were used, the product was purified by slow recrystallisation from hexane rather than filtration and washing. This yielded fine, needle-like crystals which analysis confirmed as pure $[SiO_{3/2}H]_8$ **(2)** (1.25 g, 12 % yield).[13] ^{1}H NMR ($CDCl_3$) δ 4.20 (s, Si**H**, 8H). υ_{max}/cm^{-1} (KBr disk) 2293 (s, Si-H), 1115 (s, SiO), 857 (s, Si-H), 461 (m, SiO).

Preparation of 0.2 M chloroplatinic acid solution. Chloroplatinic acid (0.820g, 2.0 mmol) was placed in a 10 cm^3 volumetric flask under a constant flow of argon. The solution was made up with dry isopropanol, capped with an argon blanket and refrigerated for storage.

Preparation of $[SiO_{3/2}CH_2CH_2C(CH_3)_2CH_2CO_2CH_3]_8$ (3). Chloroplatinic acid solution (0.2 M, 2 drops) was added to a mixture of **2** (0.427 g, 1.00 mmol), methyl-3,3-dimethyl-4-pentenoate (1.286 g, 9.0 mmol) and dry hexane (15 cm^3) under an argon atmosphere in the manner described by Feher *et al.*[3] This solution was refluxed for 3 days and the product was recovered by filtration as small, colourless cubic crystals (1.05g, 0.67 mmol, 67 % yield) which analysis confirmed as $[SiO_{3/2}CH_2CH_2C(CH_3)_2CH_2CO_2CH_3]_8$ **(3)**.[3] ^{1}H NMR ($CDCl_3$) δ 3.62 (s, O-C**H**$_3$, 24H), 2.18 (s, C**H**$_2$C=O, 16H), 1.40 (m, Si-CH_2-C**H**$_2$ 16H), 0.96 (s, C**H**$_3$, 24H), 0.57 (m, Si-C**H**$_2$, 16H). ^{13}C NMR ($CDCl_3$) δ 172.70 (O-**C**=O), 151.02 (O-**C**H_3), 44.95 ($[CH_2]_2$-**C**-$[CH_3]_2$), 35.31 (C-**C**H_2-C), 33.80 (Si-CH_2-**C**H_2), 26.48 (**C**H_3), 6.06 (Si-**C**H_2). υ_{max}/cm^{-1} (KBr disk) 2958 (m, O-CH_3), 2915 (w, CH_3 and CH_2), 2848 (w, CH_3



3

and CH_2), 1625 (s, C=O), 1396 (w, SiC), 1389 (w, CH_3), 1232 (m, C-O), 1129 (s, SiO), 468 (m, Si-O).

Attempted 3 hour hydrolysis of $[SiO_{3/2}CH_2CH_2C(CH_3)_2CH_2CO_2CH_3]_8$ using hydrochloric acid. Hydrochloric acid (37%, 25 cm^3) was added to **3** (0.100g, 0.064 mmol) and the mixture was stirred under reflux for 3 hours. On cooling, small cubic crystals of **3** were recovered by filtration (0.09g).

Attempted 3 day hydrolysis of $[SiO_{3/2}CH_2CH_2C(CH_3)_2CH_2CO_2CH_3]_8$ using hydrochloric acid (4). Hydrochloric acid (37 %, 25 cm^3) was added to **3** (0.100g, 0.064 mmol) and the mixture was stirred under reflux for 3 days. On cooling, a colourless, sparingly soluble solid was recovered by filtration (0.02 g). υ_{max}/cm^{-1} (KBr disk) 3151 (w), 2959 (vw, O-CH_3), 2954 (vw), 2896 (vw), 1797 (w), 1790 (w), 1620 (w, C=O), 1591 (w), 1546 (w), 1390 (vw, Si-C), 1382 (vw, CH_3), 1274 (w), 1244 (w, CO), 1191 (w), 1143 (s, Si-O), 1093 (m), 989 (w), 622 (w), 538 (w), 465 (s, Si-O). No satisfactory NMR data was obtained.

Attempted hydrolysis of $[SiO_{3/2}CH_2CH_2C(CH_3)_2CH_2CO_2CH_3]_8$ using 95 % sulphuric acid (5). Sulphuric acid (2 cm^3, 95 %) was added to **3** (0.100g, 0.64 mmol) and a vigorous reaction was observed resulting in an orange solution. This mixture was allowed to stand at room temperature for 1 hour before dilution with water (50 cm^3) and extraction with diethyl ether (3 × 50 cm^3). The combined organic layers were dried over magnesium sulphate and the solvent was removed under reduced pressure to yield an orange oil (0.04 g). ^1H NMR ($CDCl_3$) δ 2.18 (s, 3H), 2.10 (s, 2H).

υ_{max}/cm^{-1} (NaCl/$CDCl_3$) 3151 (w), 2959 (w, O-CH_3), 2954 (w), 1619 (vw), 1380 (vw), 1274 (w), 1191 (w), 1144 (w, Si-O), 989 (w) 465 (vw, Si-O).

Attempted hydrolysis of $[SiO_{3/2}CH_2CH_2C(CH_3)_2CH_2CO_2CH_3]_8$ using dilute sulphuric acid. Sulphuric acid (5 cm^3, 0.1 M) was added to **3** (0.100g, 0.64 mmol) and allowed to stand at room temperature for 24 hours before dilution with water (50 cm^3) and extraction with diethyl ether (3 × 50 cm^3). The combined organic layers were dried over magnesium sulphate and the solvent was removed under reduced pressure to leave unreacted **3** (0.09 g).

This experiment was repeated with the reaction mixture being refluxed for 36 hours but no reaction was observed. Further experiments were performed using a 1M acid solution, one at room temperature and the other under reflux, with no reaction being observed in either.

Attempted hydrolysis of $[SiO_{3/2}CH_2CH_2C(CH_3)_2CH_2CO_2CH_3]_8$ in acetic acid (6). 90% Acetic acid (10 cm^3) was added to a dry mixture of **3** (1.000 g, 0.64 mmol) and methane sulphonic acid (0.491 g, 5.10 mmol). This mixture was refluxed for 48 hours, diluted with water (100 cm^3) and extracted with diethyl ether (3 × 50 cm^3). Once the combined organic extracts were dried over magnesium sulphate and the solvent had been removed under reduced pressure it was found that no non-volatile material had been recovered from the reaction mixture.

An insoluble material formed during the reaction was recovered from the aqueous phase by filtration and dried in vacuo to yield a material that bore no resemblance to starting materials or the expected product (0.50 g). υ_{max}/cm^{-1} (KBr disk) 1074 (m), 799 (w), 669 (m), 591 (m), 558 (m), 465 (m, Si-O). No satisfactory NMR data was obtained.

The aqueous component was dried under reduced pressure to yield another solid which was found to be almost pure methane sulphonic acid (0.34 g).

This reaction was then repeated at room temperature with the same outcome.

2.4 Aldehyde Group Oxidation

Introduction

Many examples of hydrosilylation being used to attach functional groups to POSS substrates have been reported[22, 23, 24] and this technique was employed here to produce POSS-bearing benzaldehyde functional groups.[10] Aldehyde groups can be converted to carboxylic acid groups in a single oxidation step allowing relatively easy preparation of carboxylic acid-functionalised POSS from these benzaldehyde bearing POSS. Aldehyde-functionalised cubes have potential applications in other areas of reasearch and the development of these POSS was carried out in collaboration with Dr Paul-Alain Jaffres and Dr John Morrison who were intending to use this type of molecule as the core of a catalyst support system.[25]

As with carboxylic acid moieties, aldehyde groups can react with other substrates in the presence of hydrosilylation catalysts and some means of protection must be employed to prevent this occurring during the hydrosilylation of aldehyde derivatives to POSS. Conversion of aldehydes to dioxolanes provides adequate protection during hydrosilylation and the aldehyde can be regenerated in a single step de-protection reaction.[26, 27] Dioxolane groups are also unaffected by metallation agents making the preparation of silane derivatives from appropriately functionalised dioxolanes a simple matter (***Figure 2.3***).

Bromobenzaldehyde was selected as the aldehyde source for these experiments as the ring system provides a rigid element while the bromo group provides a convenient point at which synthetic manipulations can be performed. Both 3- and 4-bromobenzaldehyde were converted into dioxolanes and then reacted with dimethylchlorosilane to produce silanes suitable for hydrosilyation. These silanes were hydrosilylated to an octavinyl silisesquioxane $[SiO_{3/2}C_2H_3]_8$ (**7**) to yield highly functionalised silsesquioxanes which were de-protected to afford benzaldehyde-functionalised POSS.

Once the new aldehyde-functionalised POSS had been prepared and characterised, efforts were made to oxidise them to their carboxylic acid form. This was initially attempted using potassium permanganate[28] and then atmospheric oxygen. While these oxidation experiments were in progress, studies into reaction of the aldehyde bearing POSS with amines were undertaken by Jaffrès and Morrison with a view to creating pincer catalysts.[25]

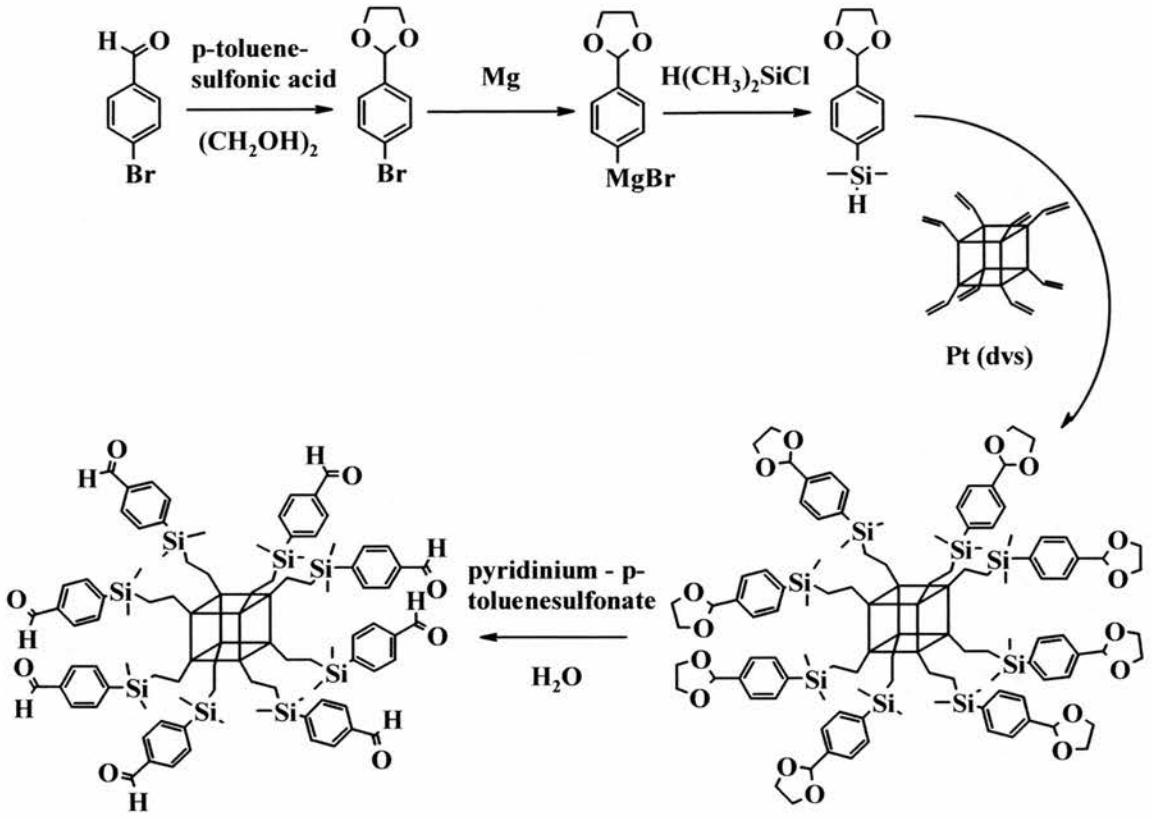
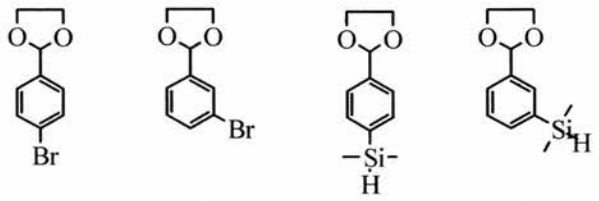


Figure 2.3. *Reaction scheme for the preparation of an aldehyde functionalised POSS from 4-bromobenzaldehyde. An identical reaction scheme using 3-bromobenzaldehyde produces the 3-isomer of the POSS.*

Results and discussion

The preparation of the silanes for hydrosilylation to the octavinyl cube proceeded as expected (***Figure 2.4***). The protection step produced 2-(4-bromo-phenyl)-[1,3]dioxolane (**8**) and 2-(3-bromo-phenyl)-[1,3]dioxolane (**9**) in yields of 85.9 and 88.0% respectively which are comparable to those reported previously.[26, 27] Grignard reagents were prepared from these dioxolanes and reacted with dimethylchlorosilane to produce 2-(4-(dimethylsilyl)phenyl)-1,3-dioxolane (**10**) and

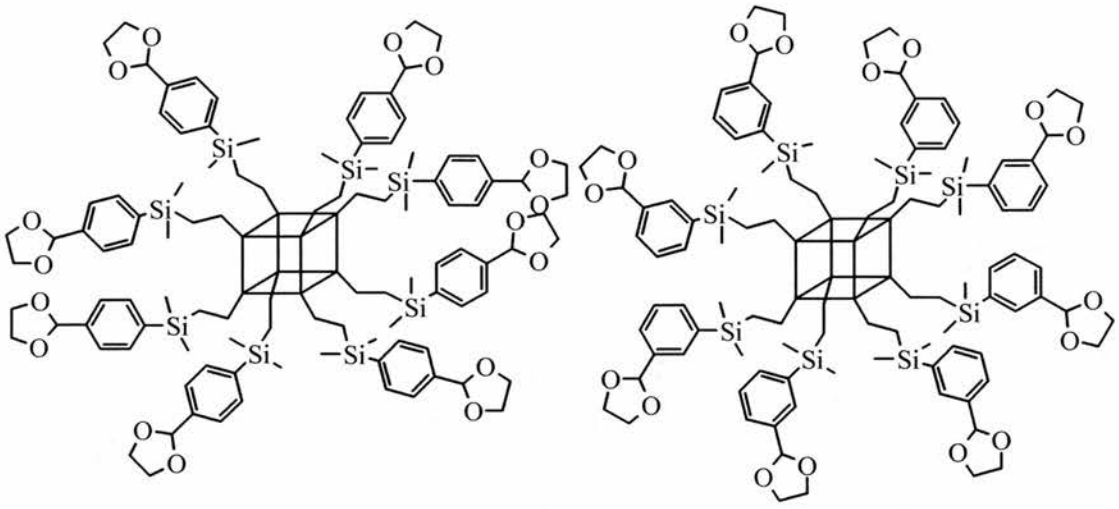
2-(3-(dimethylsilyl)phenyl)-1,3-dioxolane (**11**) in high yield. The synthesis of dioxolane **11** had not previously been reported while the preparation of **10** had, but not *via* the Grignard method described here.[29] Both **10** and **11** can be prepared using lithium reagents[30] but the Grignard method was found to be very reliable as well as simple to implement and was therefore used in preference.



8 **9** **10** **11**

Figure 2.4. *Bromobenzaldehyde derivatives* 2-(4-bromo-phenyl)-[1,3]dioxolane (***8***), 2-(3-bromo-phenyl)-[1,3]dioxolane (***9***), 2-(4-(dimethylsilyl)phenyl)-1,3-dioxolane (***10***) *and* 2-(3-(dimethylsilyl)phenyl)-1,3-dioxolane (***11***).

As expected, **10** and **11** only react through their silicon hydride group during hydrosilylation reactions catalysed by platinum (dvs), allowing them to be hydrosilylated to vinyl functionalised species such as **7** without side reactions occurring.[10] Once reaction conditions had been optimised, the preparation of 1,3,5,7,9,11,13,15-octakis{2-[4-(1,3-dioxolan-2-yl)phenyldimethylsilyl]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}] octasiloxane (**12**) and 1,3,5,7,9,11,13,15-octakis{2-[3-(1,3-dioxolan-2-yl)phenyldimethylsilyl]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}] octasiloxane (**13**) through reaction of **10** and **11** with **7** was found to be relatively straightforward (***Figure 2.5***). Essentially 100% of the vinyl groups bound to the POSS can be modified by using excess silane during the hydrosilylation reaction with the unreacted silane being removed by short path distillation when reaction is complete.



12 **13**

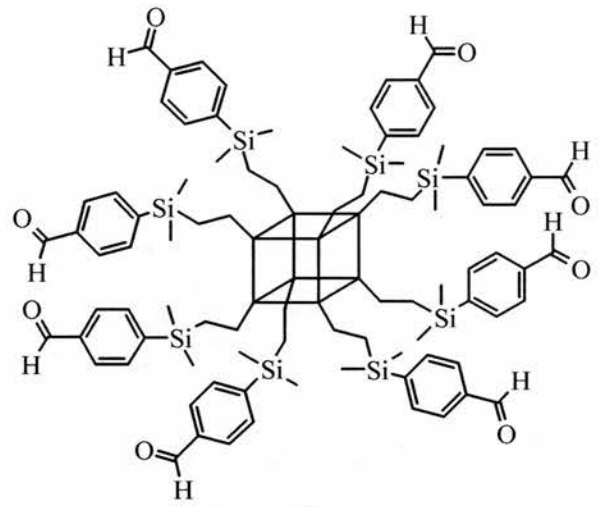
Figure 2.5. *Dioxolane-bearing POSS* ***12*** *and* ***13****.*

Platinum (dvs) was selected as the hydrosilylation catalyst as the conversion of dioxolanes to aldehydes is acid catalysed and chloroplatinic acid could promote this reaction. Despite careful selection of the catalyst however, de-protection was observed throughout these experiments and appears to occur when the dioxolanes are heated during reactions or in the subsequent work ups. The extent of the de-protection can be minimised by performing the hydrosilylation step at or below room temperature and the distillations under an effective vacuum. When a large quantity of aldehyde was present at the hydrosilylation step through partial de-protection at an earlier stage, mixed products were obtained containing both the expected moieties and an unidentified species linked to the POSS.

Despite the use of dimethylsilane groups as the silicon hydride component in the hydrosilylation reaction, mixed α and β products were obtained from this reaction. Here, α- addition refers to reaction at the terminal carbon of the vinyl group while β-

addition refers to reaction at the carbon directly attached to the cube. It was expected that the dimethylsilane components of **10** and **11** would direct the reaction towards the α carbon of the vinyl group through steric hindrance and although this does appear to be the case, in some examples nearly 25% of the silanes reacted at the β position. Initially, the hydrosilylation step was performed at reflux but reaction over a longer period at room temperature it was found that amount of β-addition can be dramatically reduced. By cooling the solution to 0 °C before addition of the catalyst and then allowing it to slowly reach to room temperature, that the amount of β-addition can be reduced to a level which cannot easily be quantified by NMR. Further cooling using a dry-ice/acetone bath at –78 °C does not produce an appreciable improvement and trace levels of β-addition are still observed.

Although elevated temperatures appear to promote conversion of the dioxlane groups to aldehydes, the dioxlane bearing POSS **12** and **13** both appear to be stable and do not undergo degradation when stored under air at room temperature. It was noted however, that trace quantities of acids in the environment could cause de-protection. Catalytic de-protection of the molecules using pyridinium p-toluenesulfonate was found to be high yielding and was used to produce the aldehyde bearing POSS molecules 1,3,5,7,9,11,13,15-Octakis{2-[4-formylphenyldimethylsilyl] ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (**14**) and 1,3,5,7,9,11,13,15-Octakis{2-[3-formylphenyldimethylsilyl]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]-octasiloxane (**15**) (***Figure 2.6***).



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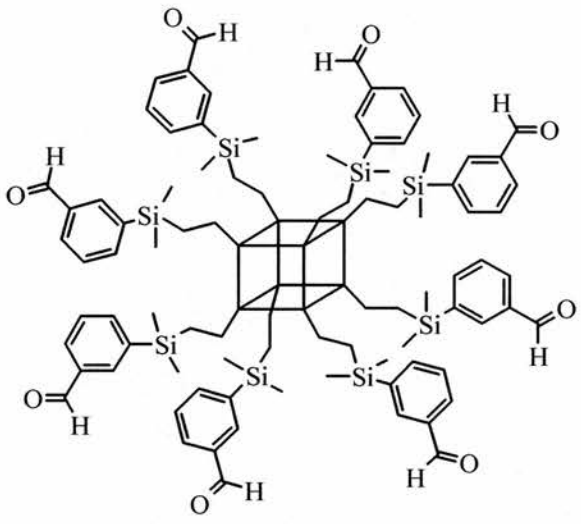

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Figure 2.6. *Benzaldehyde-bearing POSS,* 1,3,5,7,9,11,13,15-Octakis{2-[4-formylphenyldimethylsilyl] ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane ***(14)*** *and* 1,3,5,7,9,11,13,15-Octakis{2-[3-formylphenyldimethylsilyl]ethyl}-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]-octasiloxane ***(15)***.

From early studies of **14** and **15**, it appears that the aldehyde groups of both molecules remain reactive despite being bound to a POSS core. Schiff base reactions have been performed successfully with the POSS in high yields using a method based on that employed by Kuil *et al.*[30] This is only to be expected as there are several

atoms between the cube and ring system blocking any inductive effects from the silsesquioxane core that could cause the aldehyde groups to behave unusually. The dimethylsilyl group may have an effect on the reactivity of the aldehyde groups in this type of reaction, but until comparative studies have been undertaken it cannot be determined if this is the case.

It was initially thought that a synthetic procedure would have to be devised to achieve the conversion of the benzaldehyde functionalised cubes to carboxylic acid derivatives and a simple potassium permanganate reaction was selected for the first attempt. This oxidation agent proved to be too potent, resulting in cleavage of the functional groups and general degradation of the molecule. ^{1}H NMR and IR spectra suggest that the benzaldehyde groups which remain intact have been converted to carboxylic acids, but ^{13}C NMR and CHN microanalysis indicate that there are very few of these groups present in the product.

While the permanganate reactions were being performed, samples of both isomers of the aldehyde bearing POSS had been put to one side for later use and their composition was checked by ^{1}H NMR prior to the initiation of further work. It was noted that the signals from the aldehyde protons in both isomers were no longer in the correct ratio relative to the other proton resonances. Upon further investigation it was discovered that the aldehyde groups were being converted to carboxylic acids and that if a sample of the 4-benzaldehyde cube is left for a period of several months this conversion can reach almost 100% (***Figure 2.7***). As the samples were pure, it can be assumed that the oxygen uptake involves atmospheric oxygen.

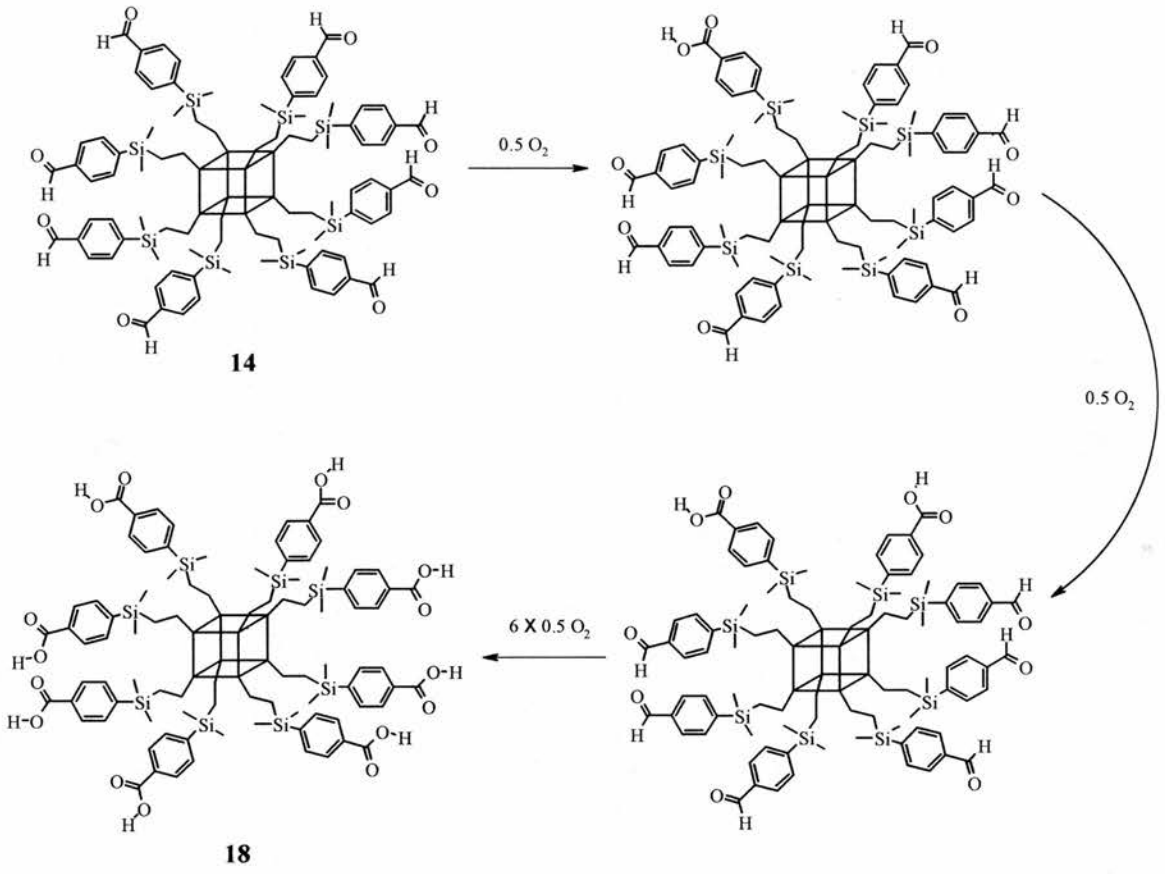


Figure 2.7. *Suggested scheme for stepwise oxidation of* ***14*** *to* ***18****. Note, the individual oxidation reactions of the last six aldehyde groups are not shown.*

The progress of the conversion can be observed using NMR as the aldehyde signal decreases in the proton spectra while an acid signal appears in the carbon spectra (***Figure 2.8***). CHN microanalysis can also be used to monitor the progress of oxidation with the percentage of oxygen present in the material increasing with time.

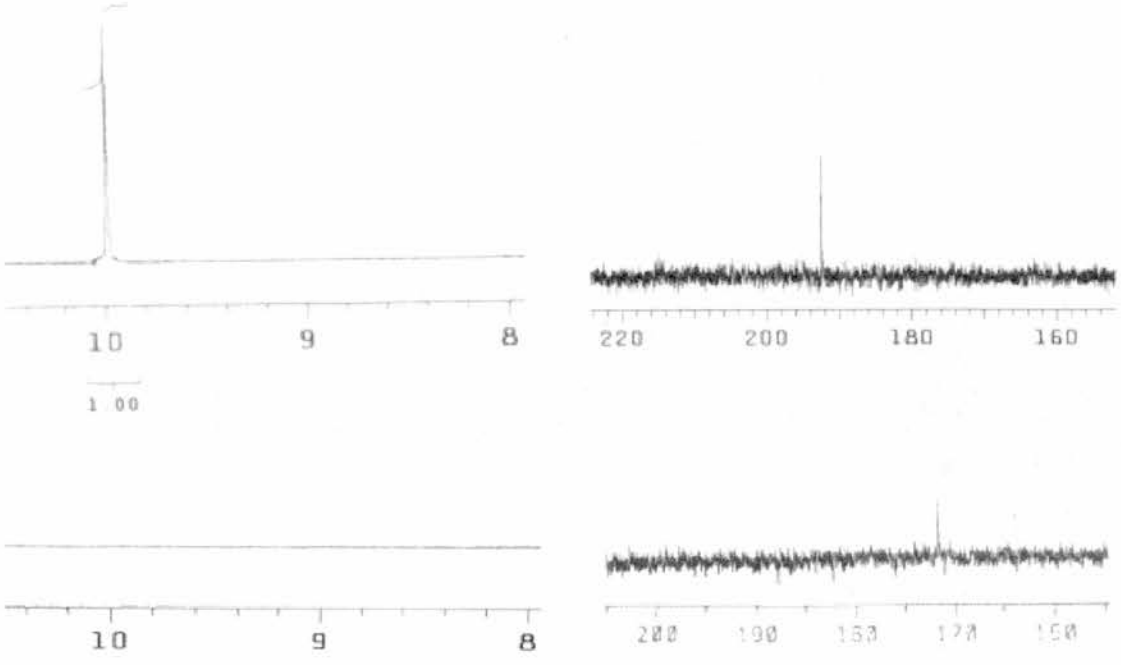


Figure 2.8. *^{1}H NMR (left) and ^{13}C NMR (right) spectra for freshly prepared* ***14*** *(top) and the same sample after 2 months of exposure to air (bottom).*

Added evidence for this process was given by the MALDITOF studies of partially oxidised samples performed in collaboration with Dr. John Morrison. These showed POSS at various stages of conversion to the carboxylic acid form with molecular ions being detected which indicated the presence of molecules in the samples with one to eight of their moieties bearing carboxylic acids (***Figures 2.9 and 2.10***).

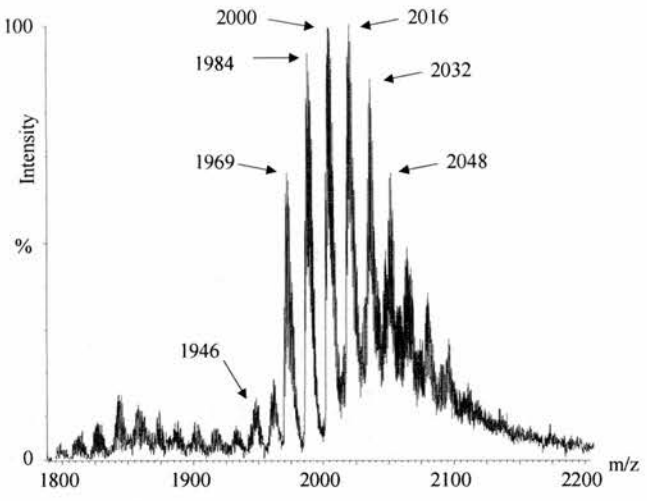


Figure 2.9. *MALDITOF spectrum of* ***14*** *oxidising to carboxylic acid 3 weeks after de-protection. The value of m/z provides an indication of the number of carboxylic acid groups present in individual POSS with higher values indicating a greater level of conversion. The stepwise increase in this value indicates that this is a stepwise process.* MALDI *m/z* 1946, (12 %) $[M - H]$,$^+$ 1969, (67), $[M - Na]$,$^+$ ($C_{88}H_{120}O_{20}Si_{16}$ requires 1944.5). 1984, (95), $[M - Na]^+$ ($C_{88}H_{120}O_{21}Si_{16}$ requires 1960.5). 2000, (99), $[M - Na]^+$ ($C_{88}H_{120}O_{22}Si_{16}$ requires 1976.5). 2016, (100), $[M - Na]^+$ ($C_{88}H_{120}O_{23}Si_{16}$ requires 1999.5). 2032, (88), $[M - Na]^+$ ($C_{88}H_{120}O_{24}Si_{16}$ requires 2015.5). 2048, (68) $[M - Na]^+$ ($C_{88}H_{120}O_{25}Si_{16}$ requires 2031.5).

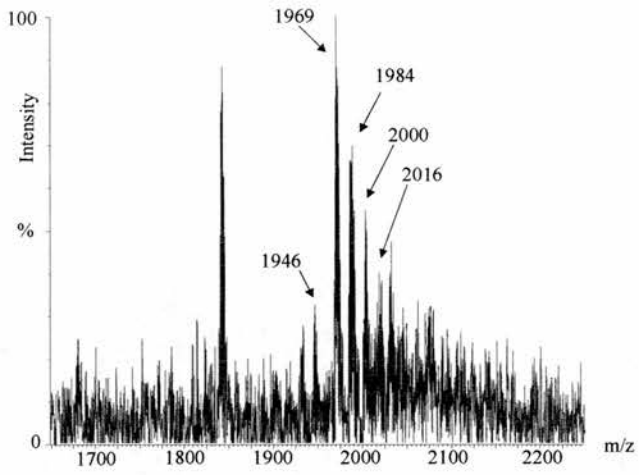


Figure 2.10. *MALDITOF spectrum for* ***15*** *7 days after de-protection. The value of m/z provides an indication of the number of carboxylic acid groups present in individual POSS with higher values indicating a greater level of conversion. The stepwise increase in this value indicates that this is a stepwise process.* MALDI *m/z* 1946, (33 %) $[M - H]^+$ 1969, (100), $[M - Na]^+$ ($C_{88}H_{120}O_{20}Si_{16}$ requires 1944.5). 1984, (70), $[M - Na]^+$ ($C_{88}H_{120}O_{21}Si_{16}$ requires 1960.5). 2000, (54), $[M - Na]^+$ ($C_{88}H_{120}O_{22}Si_{16}$ requires 1976.5). 2016, (40), $[M - Na]^+$ ($C_{88}H_{120}O_{23}Si_{16}$ requires 1999.5).

POSS **14** and **15** are soluble in many solvents and partially oxidised cubes remain soluble in chloroform until between 60 and 80% of the aldehyde units have been converted. Above this level, the POSS are effectively insoluble in chloroform and many other solvents with only warm methanol offering the possibility of solvation. It was also noted that samples of the POSS become more crystalline in appearance as the number of aldehyde groups decreases and acid groups increases. Newly prepared **14** is recovered as a waxy solid while **15** has only been recovered as a very viscous oil but both undergo this change in appearance. No crystals of either **18**

or **19** were grown however as their insolubility hindered the optimisation of the re-crystallising medium.

To obtain pure samples of **14** and **15** it is crucial to remove all of the excess silane from the hydrosilylation reaction before performing the de-protection step. As soon as this material and the groups attached to the silsesquioxane core began to oxidise it becomes impossible to remove the silane component, presumably because of hydrogen bonding between the silane and oxidised POSS moieties.

While **14** oxidises smoothly to the acid form, **15** appears to undergo fragmentation or decomposition, even when left to oxidise at room temperature. NMR spectra obtained from samples of **15** undergoing conversion contained several unidentified peaks while MALDITOF detected unusual fragmentation components that did not match any of the expected products. It was found to be impossible to separate the decomposition products from the bulk of the material to allow detailed investigation, presumably due to hydrogen bonding between carboxylic acid groups of the fragments and those of the bulk material. The insolubility of the acid product prevented separation by chromatography, while heating under reduced pressure removed no low or intermediate molecular weight components below 150 °C (0.2 mmHg) with higher temperatures causing decomposition of the material.

The oxidation of the benzaldehyde functionalities of **14** and **15** in air was rapid but it was not clear how this compared with the rate of oxidation of 3- and 4-bromobenzaldehyde. For convenience, the rates of oxidation of 3- and 4-bromobenzaldehyde were compared with those of the de-protected forms of **10** and **11**

rather than **14** and **15**. It was expected that these aldehydes would behave in a similar manner to benzaldehyde groups attached to a POSS core as the ethyl linkage found in the cube variants would inhibit or at least reduce any inductive effect from the cube.

To ensure that a comparison could safely be made between the oxidation rates of all four aldehydes, parallel experiments were performed under identical conditions. A small portion of each aldehyde was left to oxidise in air for 10 days with the extent of oxidation being monitored through NMR using the difference in peak area between the aromatic proton resonances and those of the aldehyde groups (***Figure 2.11***).

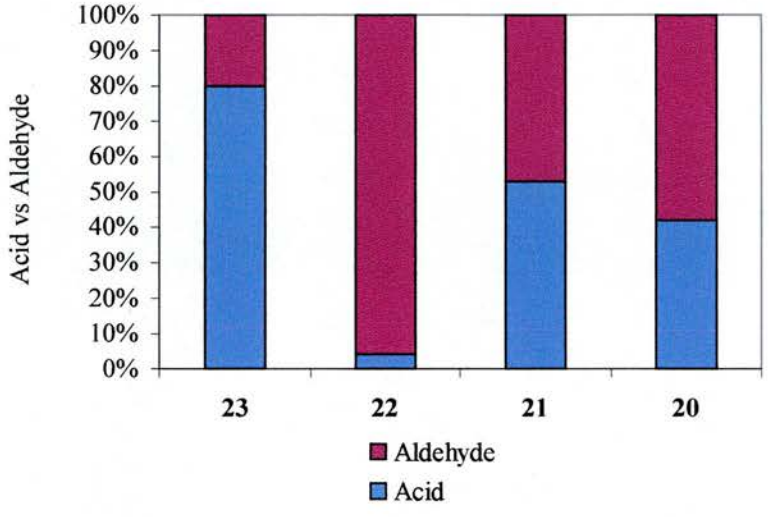


Figure 2.11. *Progress of atmospheric oxidation of 3-bromobenzaldehyde (**23**), 4-bromobenzaldehde (**22**), 3-dimethylsilylbenzaldehyde (**21**) and 4-dimethylsilylbenzaldehyde (**20**) after 10 days.*

In the case of 3-bromobenzaldehyde, 80 % of the aldehyde groups were converted to carboxylic acid groups over the 10 day period while only 4% of the 4-bromobenzaldehyde was converted to the acid form. Over the same period, it was observed that 53% of the de-protected **10** and 42% of the de-protected **11** were

converted into the acid forms. It is clear from these results that both the type and the position of substituents attached to the aromatic ring affect the rate of aldehyde oxidation. It would appear that substituents with an electron withdrawing character promote oxidation when in the 3- position but stabilise the aldehyde group when in the 4- position. Groups with electron donating properties have the opposite effect with the 4- isomer oxidising faster than the 3-. This has implications for future studies where benzaldehyde moieties may be linked to POSS to serve as precursors for further reactions. For example, Schiff base condensations require pure aldehydes as starting materials and it would therefore be better to use a 4-benzaldehyde isomer linked directly to a POSS core rather than the 3- form as the electron withdrawing properties of the core should reduce the rate of oxidation.

The mechanism of oxidation was not studied but it has been suggested that benzaldehydes oxidise in air through a radical type reaction promoted by light and the presence of moisture.[31] As the oxidation process observed here appears to be spontaneous this may indeed be the mechanism that is active. Future studies could investigate this further by simply keeping some samples of the aldehyde-functionalised POSS in the dark while exposing others to daylight. If there is a difference in oxidation rate then the suggested radical mechanism may be operating. c

Conclusions

It has been demonstrated that two benzaldehyde functionalised POSS can be prepared from the 3- and 4-isomers of bromobenzaldehyde. These molecules are both

capable of further reactions making them potentially useful starting materials for a number of applications, in particular as dendrimer cores.

Oxidising these molecules produces carboxylic acid-functionalised POSS that have the potential to form extended POSS networks when conditions can be found to encourage this. In the case of the **14**, the best way to convert it to the acid form is simply to allow it to oxidise in air. This avoids using reagents or conditions which could degrade the molecule and as long as the aldehyde sample is pure, the product should require no purification. As **15** appears to undergo fragmentation over time it would be prudent to find a reaction to accelerate the oxidation process and a means to stabilise the product. If the fragmentation is a side effect of the oxidation process however, it may not be possible to fully oxidise the molecule without degrading it.

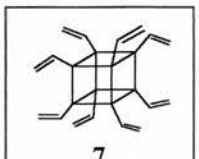
Since carboxylic acid functionalised cubes have been synthesised, attempts can now be made to prepare networks from them. Efforts were made to dissolve POSS **18** and **19** in a range of common solvents but, at best, only partial solvation was achieved. This will probably hamper efforts to prepare networks at room temperature using systems such as the zinc (II) method demonstrated by Yaghii *et al* which uses a solution of the acid species.[32] As yet, no attempts have been made to investigate the properties of these molecules under elevated temperatures and pressures which may increase the solubility of the compound in the reaction medium. Such conditions could be achieved using an autoclave type arrangement and could allow various self-assembly techniques to be attempted ranging from simple hydrogen bonding between the POSS to more elaborate metal co-ordination.[33]

Whether or not networks can be assembled from the carboxylic acid bearing POSS, the aldehyde forms have already been used as precursors in Schiff Base reactions and show promise as dendrimer cores.[24] As aldehydes can be synthetically manipulated in many different ways, it is anticipated that both **12** and **13** will prove to be useful synthetic precursors.

Experimental

General. Trichlorovinylsilane (Aldrich), toluene (Ultrafine), 3-bromobenzaldehyde (Aldrich), 4-bromobenzaldehyde (Lancaster), ethylene glycol (Avocado), *p*-toluenesulphonic acid (Lancaster), diethyl ether for work ups (BDH), magnesium sulphate (Fisher), sodium hydrogen carbonate (Fisher), magnesium turnings (Lancaster), dimethylchlorosilane (Aldrich), iodine (Fisher), nitrogen (BOC), argon (BOC), platinum divinyltetramethyl disiloxane complex in xylene [2.1-2.4 % platinum concentration] (Aldrich), pyridinium p-toluenesulphonate (Lancaster) and acetone (Bamford Laboratories) were all used as supplied. Diethyl ether (BDH) for hydrosilylation was distilled from sodium (Fisons) under a nitrogen atmosphere prior to use. Information on the analytical equipment and techniques is provided in **Appendix B**.

Preparation of $[SiO_{3/2}C_2H_3]_8$ (7). Trichlorovinylsilane (50.8 g, 315 mmol) was added to an ice-cold solution of acetone (1500 cm^3) and water (450 cm^3) *via* a dropping funnel over a 45 minute period. The resultant mixture was allowed to reach room temperature and was then stirred for 6



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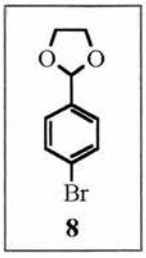
weeks. The product was recovered by filtration and dried to yield a white powder (5.65 g, 23 %) which analysis confirmed as the vinyl-functionalised POSS $[SiO_{3/2}C_2H_3]_8$ (**7**) reported by Voronkov *et al.*[9] ^{1}H NMR ($CDCl_3$) δ 6.14 - 5.82 (m, C**H**=C**H**$_2$, 24H). ^{13}C NMR ($CDCl_3$) δ 137.02 (-C=CH_2), 128.69 (-C=CH_2). ν/cm^{-1} (KBr disk) 3025 (w), 2986 (w), 2961 (m), 1945 (w), 1604 (m, C=C), 1409 (s), 1277 (s), 1111 (vs, Si-O), 1004 (s, CH=CH_2), 968 (s, CH=CH_2), 778 (s), 704 (w), 573 (s), 463 (m, Si-O).

Preparation of 2-(4-Bromo-phenyl)-[1,3]dioxolane (8). Toluene (200 cm^3) was added to 4-bromobenzaldehyde (40.60g, 219 mmol), ethylene glycol (18.12 g, 292 mmol) and *p*-toluenesulphonic acid (0.60g, 3.15 mmol). The resultant mixture was stirred and refluxed overnight under Dean-Stark conditions in the manner described by Zhung *et al.*[26] On cooling, the toluene was removed from the reaction mixture by rotary evaporation and the residue diluted with diethyl ether (150cm^3). The solution was washed with aqueous sodium hydrogen carbonate solution (50 cm^3, 1M) followed by a saturated brine (2 × 50 cm^3) and then dried using magnesium sulphate. After filtration, the product was purified by reduced pressure distillation (84 °C, 0.2 mmHg) to yield a clear, colourless oil which analysis confirmed as 2-(4-Bromo-phenyl)-[1,3]dioxolane (38.03 g, 86 % yield).[26] ^{1}H NMR ($CDCl_3$) δ 7.53 (d, J_{HH}=8.5 Hz, C**H**, 2H) 7.38 (d, J_{HH}=8.5 Hz, C**H**, 2H), 5.79 (s, O-C**H**-O, 1H). 4.10 (m, O-C**H**$_2$-C**H**$_2$-O, 4H). ^{13}C NMR ($CDCl_3$) δ 137.02 (**C**-C), 131.49 (**C**-H), 128.21 (**C**-H), 123.25 (**C**-Br), 103.08 (O-**C**H-O), 65.35 (O-**C**H$_2$-**C**H$_2$-O). ν_{max}/cm^{-1} (NaCl) 2953 (s, CH), 2882 (s, CH), 2834 (s, CH), 2771 (m), 2726 (w), 2680 (w), 2636 (w), 2583 (w), 2483 (vw), 2280 (vw), 2118 (m), 1955 (w), 1987 (w), 1826 (vw), 1773 (vw), 1709 (m), 1699 (s), 1597 (m, aryl C), 1588 (m,



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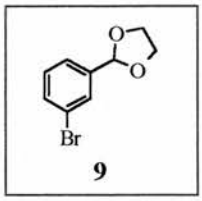
aryl C), 1475 (s, aryl C), 1447 (m), 1420 (s), 1378 (s), 1365 (s), 1312 (m), 1251 (s), 1221 (s), 1173 (m), 1121 (s, C-O), 1084 (s, C-O), 1030 (s), 967 (s), 945 (s), 888 (vs, CH), 836 (s), 796 (s), 764 (s), 736 (s), 709 (s, CH), 652 (s, C-Br), 629 (s), 552 (w), 495 (w).

Preparation of 2-(3-Bromo-phenyl)-[1,3]dioxolane (9).



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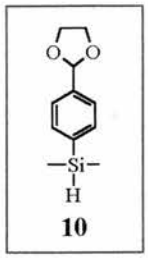
Toluene ($200cm^3$) was added to 3-bromobenzaldehyde (35.07g, 190 mmol), ethylene glycol (14.10g, 227 mmol) and *p*-toluenesulphonic acid (0.55g, 2.89 mmol). The resultant mixture was stirred and refluxed overnight under Dean-Stark conditions in the manner described by Zhung *et al.*[26] On cooling, the toluene was removed from the reaction mixture by rotary evaporation and the residue diluted with diethyl ether ($150cm^3$). The solution was washed with aqueous sodium hydrogen carbonate solution ($50\ cm^3$, 1M) followed by saturated brine ($2 \times 50\ cm^3$) and then dried using magnesium sulphate. After filtration, the product was purified by reduced pressure distillation (84 °C, 0.2 mmHg) to yield a clear, colourless oil which analysis confirmed as 2-(3-Bromo-phenyl)-[1,3]dioxolane (38.20 g, 88 % yield).[26] ^{1}H NMR ($CDCl_3$) δ 7.71 (m, C**H**, 1H), 7.52 (m, C**H**, 1H), 7.43(m, C**H**, 1H), 5.80 (s, O-C**H**-O, 1H), 4.03 (m, O-C**H**$_2$-C**H**$_2$-O, 4H). ^{13}C NMR ($CDCl_3$) δ 140.24 (**C**-CH), 133.48 (**C**H), 129.18 (**C**H), 128.35 (**C**H), 126.42 (**C**H), 122.47 (**C**Br), 103.76 (O-**C**H-O), 65.32 (O-**C**H$_2$-**C**H$_2$-O). ν_{max}/cm^{-1} (NaCl) 2953 (m, CH), 2886 (s, CH,), 2736 (m), 2677 (w), 2634 (w), 2579 (vw), 2360 (w), 2334 (w), 1948 (w), 1879 (vw), 1867 (w), 1722 (w), 1699 (w), 1585 (w), 1573 (s, aryl C), 1475 (s, aryl C), 1435 (s, aryl C), 1377 (s, CH), 1346 (m), 1277 (m), 1262 (s), 1211 (s), 1100 (vs, C-O), 1069 (vs, C-O), 1028 (s), 991 (s), 966 (s), 942 (s), 882 (s, CH), 785 (vs, CH), 749 (m), 710 (m, CH), 697 (s, CBr), 672 (m), 630 (w), 561 (w), 499 (w), 486 (w), 460 (m).



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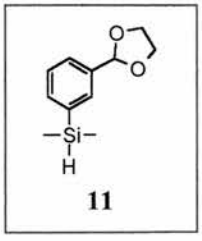
Preparation of 2-(4-(dimethylsilyl)phenyl)-1,3-dioxolane (10). Dry THF (10 cm^3) was added to the magnesium turnings (4.61g, 190 mmol) and a single crystal of iodine under an argon atmosphere. **8** (38.03 g, 166 mmol) was dissolved in dry THF (190 cm^3) and added drop-wise to the magnesium turnings with vigorous stirring. The mixture rapidly turned black and was allowed to stir for and additional 2 hours before being added slowly *via* a cannula to a solution of dimethylchlorosilane (18.24 g, 192 mmol) dissolved in THF (100 cm^3) under argon. After stirring for 4 hours, the resultant mixture was added to aqueous sodium hydrogen carbonate solution (50 cm^3, 1 M), extracted with diethyl ether (3 × 50 cm^3) and the combined organic layers were dried over magnesium sulphate. After filtration the solvents were removed by rotary evaporation and the product was purified by reduced pressure distillation (82 °C, 0.2 mmHg) to give a clear, colourless oil (13.15 g, 38 % yield). ^{1}H NMR ($CDCl_3$) δ 7.61 (d, J_{HH}=8.0 Hz, C**H**, 2H), 7.51 (d, J_{HH}=8.0 Hz, C**H**, 2H), 5.86 (s, OC**H**O, 1H), 4.47 (sept, J_{HH}=3.8Hz, Si**H**, 1H), 4.15 (m, O-C**H**$_2$-C**H**$_2$-O, 4H), 0.38 (d, J_{HH}=3.8Hz, Si-C**H**$_3$, 6H). ^{13}C NMR ($CDCl_3$) δ 138.89 and 138.72 (**C**-Si and **C**-CH), 134.10 (**C**H), 125.80 (**C**H), 103.68 (O-**C**H-O), 65.35 (O-**C**H$_2$-**C**H$_2$-O), -3.75 (Si-**C**H$_3$). ν $_{max}$/cm^{-1} (NaCl) 3073 (m), 3025 (m), 2942 (s, CH), 2880 (s, CH), 2124 (vs, SiH), 1410 (s), 1390 (s, SiC), 1310 (m), 1245 (s, Si-CH_3), 1223 (s), 1178 (m, C-O), 1083 (s, C-O), 1022 (m), 970 (m), 944 (m), 882 (s, CH), 813 (s, Si-CH_3), 770 (s), 712 (m, CH), 625 (m). CHN Microanalysis: Found 63.15 % C, 8.16 % H; Calculated 63.42 % C, 8.14 % H.



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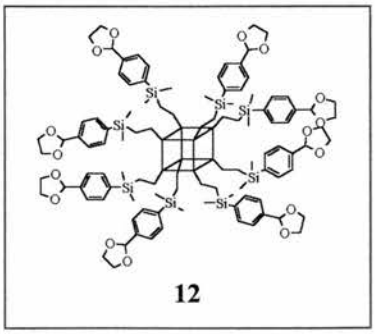
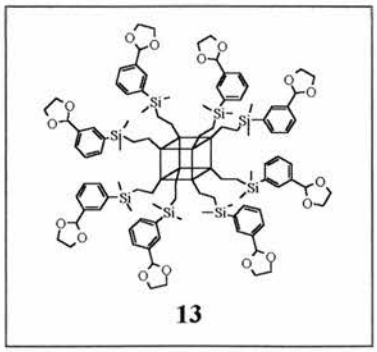
Preparation of 2-(3-dimethylsilylphenyl)-1,3-dioxolane (11). Dry THF (10 cm^3) was added to the magnesium turnings (4.44g, 183 mmol) and a single crystal of iodine under an argon atmosphere. **9** (37.09 g, 162 mmol) was dissolved in dry THF (190 cm^3) and added drop-wise to the magnesium turnings with vigorous stirring. The mixture rapidly turned black and was allowed to stir for and additional 2 hours before being added slowly *via* a cannula to a solution of dimethylchlorosilane (19.05 g, 201 mmol) dissolved in THF (100 cm^3) under argon. After stirring for 4 hours, the resultant mixture was added to aqueous sodium hydrogen carbonate solution (50 cm^3, 1 M), extracted with diethyl ether (3 × 50 cm^3) and the combined organic layers were dried over magnesium sulphate. After filtration the solvents were removed by rotary evaporation and the product was purified by reduced pressure distillation (83 °C, 0.2 mmHg) to give a clear, colourless oil (18.34 g, 48 % yield). ^{1}H NMR ($CDCl_3$) δ 7.72 (s, C**H**, 1H), 7.61 (m, C**H**, 1H), 7.56 (m, C**H**, 1H), 7.44 (m, C**H**, 1H), 5.84 (s, C**H**, 1H), 4.49 (sept, J_{HH}=3.8, Si**H**, 1H), 4.13 (m, O-C**H**$_2$-C**H**$_2$-O, 4H), 0.39 (d, J_{HH}=3.7 Hz, Si-C**H**$_3$, 6H). ^{13}C NMR ($CDCl_3$) δ 137.73 and 137.08 (Si-**C** and **C**-CH), 134.95 (**C**H), 131.99 (**C**H), 127.90 (**C**H), 127.35 (**C**H), 103.92 (O-**C**H-O), 65.37 (O-**C**H$_2$-**C**H$_2$-O), -3.73 (Si-**C**H$_3$). ν_{max}/cm^{-1} (NaCl) 2959 (m, CH), 2888 (m, CH), 2764 (w), 2584 (vw), 2288 (vw), 2117 (vs, Si-H), 1918 (w), 1703 (s), 1665 (w), 1597 (m, aryl C), 1558 (w, aryl C), 1474 (m, aryl C), 1410 (s, CH), 1368 (s, Si-C), 1310 (s), 1251 (s), 1217 (s), 1114 (s, C-O), 1080 (vs, C-O), 1030 (m), 972 (s), 945 (s), 881 (s, CH), 834 (s, Si-CH_3), 797 (m, CH), 766 (m), 652 (m), 629 (m), 533 (w). CHN Microanalysis: Found 63.13 % C, 8.14 % H; Calculated 63.42 % C, 8.14 % H.

Preparation of 1,3,5,7,9,11,13,15-octakis{2-[4-(1,3-dioxolan-2-yl)phenyldimethylsilyl]ethyl}pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (12). **10** (6.433 g, 308.8 mmol) and **7** (2.20 g, 3.48 mmol) were dissolved in diethyl ether (50 cm^3) under an atmosphere of argon and the solution was cooled in an ice bath. Platinum (dvs) (2.1-2.4 % platinum concentration in xylene, 10 drops) was added to the solution which was slowly returned to room temperature. The reaction mixture was stirred overnight and then passed through a silica gel pad (200-240 mesh, diethyl ether). The solvent was removed from the filtrate by rotary evaporation and the excess **10** was removed by short path distillation (100 °C, 0.2 mmHg to yield the product as a viscous oil which solidified at room temperture (7.64 g, 95 % yield). ^{1}H NMR ($CDCl_3$) δ 7.53 (d, J_{HH}=8.0 Hz, C**H**, 16H), 7.47 (d, J_{HH}=8.0 Hz, C**H**, 16H), 5.82 (m, O-C**H**-O, 8H), 4.10 (m, O-C**H**$_2$-C**H**$_2$-O, 32 H), 0.82 (m, C**H**$_2$, 16H), 0.57 (m, Si-C**H**$_2$, 16H), 0.29 (s, C**H**$_3$, 48H). ^{13}C NMR ($CDCl_3$) δ 140.38 and 138.50 (2s, **C**-Si and **C**-CH), 133.70 (**C**H), 125.68 (**C**H), 103.73 (O-**C**H-O), 65.32 (O-**C**H$_2$-**C**H$_2$-O), 7.04 (-**C**H$_2$-), 4.48 (-**C**H$_2$-), -3.49 (Si-**C**H$_3$). ν max/cm^{-1} (NaCl) 2958 (m, CH), 2890 (m, CH), 1408 (m), 1251 (m, Si-CH$_3$), 1116 (vs, Si-O), 1022 (m), 971 (m), 944 (m), 839 (m), 815 (m, Si-CH$_3$). CHN Microanalysis: Found 54.87 % C, 6.71 % H; Calculated 54.32 % C, 6.66 % H.



12

Preparation of 1,3,5,7,9,11,13,15-octakis{2-[3-(1,3-dioxolan-2-yl)phenyldimethylsilyl]ethyl}pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (13). **11** (1.573 g, 7.55 mmol) and **7** (0.509 g, 0.80 mmol) were dissolved in diethyl ether (25 cm^3) under an argon atmosphere

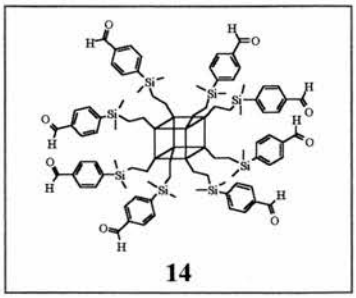


13

and the resultant solution was cooled in an ice bath. Platinum (dvs) (2.1-2.4 % platinum concentration in xylene, 10 drops) was added to the solution which was slowly returned to room temperature. The reaction mixture was stirred overnight and then passed through a silica gel pad (200-240 mesh, diethyl ether). The solvent was removed from the filtrate by rotary evaporation and the excess **11** was removed by short path distillation (100 °C, 0.2 mmHg to yield the product as a viscous oil which solidified at room temperture (1.62 g, 88 %). ^{1}H NMR ($CDCl_3$) δ 7.59 (s, C**H**, 8H), 7.50 (m, C**H**, 8H), 7.45 (m, C**H**, 8H), 7.34 (m, C**H**, 8H), 5.81 (s, C_2C**H**, 8H), 4.10 (m, O-C**H**$_2$-C**H**$_2$-O, 32H), 0.76 (m, C-C**H**$_2$, 16H), 0.54 (m, Si-C**H**$_2$, 16H), 0.28 (s, Si-C**H**$_3$, 48H). ^{13}C NMR ($CDCl_3$) 139.37 and 136.94 (2s, **C**-Si and **C**-CH), 134.64 (**C**H), 131.68 (**C**H), 127.81 (**C**H), 126.93 (**C**-H), 103.98 (O-**C**H-O), 65.32 (O-**C**H$_2$-**C**H$_2$-O), 7.08 (-**C**H$_2$-), 4.52 (-**C**H$_2$-), -3.49 (Si-**C**H$_3$). ν/cm^{-1} ($CDCl_3$) 2957 (m, CH), 2890 (m, CH), 1408 (m), 1251 (m), 1116 (vs, Si-O), 1022 (m), 971 (m), 944 (m), 839 (m, Si-CH_3), 815 (m). CHN Microanalysis: Found 55.32 % C, 6.57 % H; Calculated 54.32 % C, 6.66 % H.

Early experiments were performed with room temperature addition of the catalyst and overnight refluxing of the reaction mixture resulting in significant β–addition occurring. ^{1}H NMR ($CDCl_3$) δ 7.71 (s, C**H**, β-addition), 7.59 (s, C**H**, α-addition), 7.55 (m, C**H**, β-addition), 7.50 (m, C**H**), 7.45 (m, C**H**), 7.41 (m, C**H**, β-addition), 7.34 (m, C**H**, α-addition), 5.88 (s, C_2C**H**, β-addition), 5.81 (s, C_2C**H**, α-addition), 4.10 (m, O-C**H**$_2$-C**H**$_2$-O), 0.76 (m, C-C**H**$_2$, α-addition), 0.54 (m, Si-C**H**$_2$, α-addition), 0.42 (m, C-CH_3, β-addition) 0.28 (s, Si-C**H**$_3$) 0.12 (m, CH, β-addition).

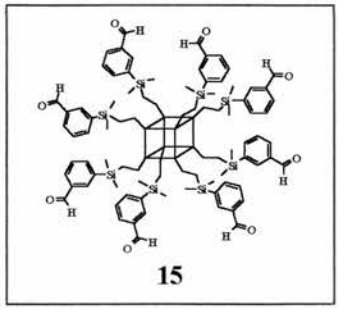
Preparation of 1,3,5,7,9,11,13,15-octakis{2-[4-formylphenyldimethylsilyl] ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (14).



14

12 (1.74 g, 0.75 mmol), pyridinium p-toluenesulfonate (0.47 g, 1.86 mmol) and wet acetone (35 cm^3) were refluxed overnight. On cooling, the solvent was removed under reduced pressure and the product was re-dissolved in diethyl ether (50 cm^3). This solution was washed with aqueous sodium hydrogen carbonate (1M, 2 × 50 cm^3) followed by brine (50 cm^3) and the organic component was dried over magnesium sulphate. After filtering, the solvent was removed under reduced pressure and the product was recovered as a viscous oil which solidified at room temperature (1.09 g, 75 % yield). ^{1}H NMR ($CDCl_3$) δ 9.99 (s, C**H**O, 8H), 7.77 (d, J_{HH}=7.9 Hz, C**H**, 16H), 7.59 (d, J_{HH}=7.9 Hz, C**H**, 16H), 0.74 (m, C**H**$_2$, 16H), 0.49 (m, C**H**$_2$, 16H), 0.25 (s, Si-C**H**$_3$, 48H). ^{13}C NMR ($CDCl_3$) δ 192.46 (-**C**HO), 147.52 (-**C**-CHO), 136.64 (**C**H), 134.01 (**C**H), 128.60 (**C**-Si), 6.69 (**C**H$_2$), 4.18 (**C**H$_2$), -3.98 (Si-**C**H$_3$), 4.34 (-**C**H$_2$-), 7.01 (-**C**H$_2$-). ν_{max}/cm^{-1} (NaCl) 2955 (m, CH), 2892 (m, CH), 1704 (s, CHO), 1597 (m), 1558 (m), 1407 (m), 1383 (m, Si-C), 1251 (m, Si-CH$_3$), 1213 (m), 1103 (vs, Si-O), 837 (m), 812 (m, Si-CH$_3$), 759 (m), 692 (m), 551 (m). CHN Microanalysis: Calculated 54.28 % C, 6.21 % H; Found 53.32% C, 6.31 % H.

Preparation of 1,3,5,7,9,11,13,15-Octakis{2-[3-formylphenyldimethylsilyl] ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (15).



15

13 (2.240g, 0.97 mmol), pyridinium p-toluenesulfonate (0.480 g, 1.90 mmol) and wet acetone (40 cm^3) were

refluxed overnight. The solvent was removed under reduced pressure and diethyl ether (50 cm^3) was used to re-dissolve the residue. This solution was washed with aqueous sodium hydrogen carbonate solution (1M, 2 × 50 cm^3) followed by brine (50 cm^3) and the organic component was then dried over magnesium sulfate. After filtration, the solvent was removed under reduced pressure to give a viscous, colourless oil (1.74 g, 92 %). ^{1}H NMR ($CDCl_3$) δ 10.03 (s, C**H**O, 8H), 7.99 (s, C**H**, 8H), 7.85 (m, C**H**, 8H), 7.71 (m, C**H**, 8H), 7.48 (m, C**H**, 8H), 0.78 (m, C$\mathbf{H}_2$, 16H), 0.53 (m, C$\mathbf{H}_2$, 16H), 0.28 (s, Si-C$\mathbf{H}_3$, 48H). ^{13}C NMR ($CDCl_3$) δ 192.68 (-**C**HO), 140.42 (-**C**-CHO), 139.51 (**C**-Si), 135.60 (**C**H), 134.61 (**C**H), 130.56 (**C**H), 128.40 (**C**H), 7.01 (-**C**H_2-), 4.34 (-C$\mathbf{H}_2$-), -3.66 (Si-**C**H_3). ν max/cm^{-1} (NaCl) 2951 (m, CH), 2888 (m, CH), 1696 (s, C-CHO), 1586 (m), 1407 (m), 1370 (m, Si-CH_3), 1249 (m, Si-CH_3), 1206 (m), 1101 (vs), 896 (m), 870 (m), 836 (m, Si-CH_3), 754 (m), 692 (m), 650 (m), 545 (m). C-H-N Microanalysis: Found 54.75 % C, 6.49 % H; Calculated 54.28 % C, 6.21 % H.

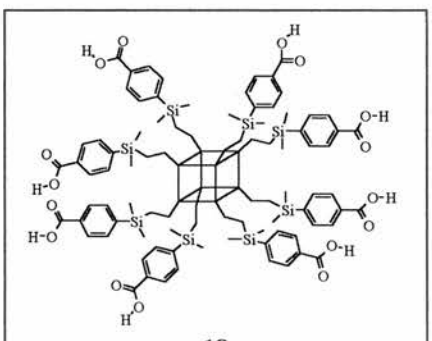
Quantities of **13** with a high degree of β addition can be de-protected in the manner described above to produce molecules with mixed isomer functional groups. ^{1}H NMR ($CDCl_3$) δ 10.03 (s, C**H**O, β-addition), 10.01 (s, C**H**O, α-addition), 8.04 (s, C**H**, β-addition), 8.00 (s, C**H**, α-addition), 7.89 (m, C**H**, β-addition), 7.84 (m, C**H**, α-addition), 7.79 (m, C**H**, β-addition), 7.54 (m, C**H**, β-addition), 7.49 (m, C**H**, α-addition), 0.78 (m, C$\mathbf{H}_2$, α-addition), 0.69 (s, C**H**, 0.54 β-addition), (m, C$\mathbf{H}_2$, α-addition), 0.42 (m, C-C$\mathbf{H}_3$, β-addition), 0.28 (s, Si-C$\mathbf{H}_3$, α-addition), 0.13 (m, Si-C$\mathbf{H}_3$, β-addition). ^{13}C NMR ($CDCl_3$) δ 192.68 (broadened, (**C**HO), 140.42 (**C**-CHO), 139.51 (**C**-Si, α-addition), 138.98 (**C**-Si, β-addition), 135.60 (**C**H, α-addition), 135.55

(**C**H, β-addition), 134.61 (**C**H, α-addition), 134.59 (**C**H, β-addition), 134.360 (**C**H, β-addition)130.56 (**C**H, α-addition), 130.54 (CH, β-addition), 128.40 (**C**H, α-addition), 128.39 (**C**H, β-addition), 7.01 (-**C**H_2-, α-addition), 4.43 (-**C**H_2-, α-addition), 1.05 (**C**H, β-addition), 0.75 (C-**C**H_3, β-addition), -3.54 (Si-**C**H_3, β-addition), -3.66 (Si-**C**H_3, α-addition).

Potassium permanganate oxidation of 1,3,5,7,9,11,13,15-Octakis{2-[4-formylphenyldimethylsilyl] ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (16). Potassium permanganate (0.68 g, 4.31mmol) in acetone (20 cm^3) was added drop-wise to a solution of **14** (1.090 g, 0.53 mmol) in acetone (5 cm^3). During the addition, an exotherm was observed. Once all the permanganate had been added, the solution was stirred for a further 2 hours and the solvent was removed by heating under reduced pressure. The resultant solid was extracted using hot methanol (3 × 100 cm^3) which was then removed under reduced pressure to leave a mixture of products (0.36 g). ^{1}H NMR (CD_3OD) δ 8.46 (s), 7.87 (d, J_{HH}=8.3 Hz, C**H**, 2H), 7.42 (d, J_{HH}=8.3 Hz, C**H**, 2H), 5.44 (s), 3.80 (s), 3.58 (s), 2.11 (m), 0.79 (broad s, C**H**$_2$, 2H), 0.27 (broad s, C**H**$_2$, 2H), 0.11 (broad s, Si-C**H**$_3$, 6H) Based on the assumption that less than 100 % of the functional groups bound to the POSS are benzoic acid type groups. ^{13}C NMR (CD_3OD) δ 136.66, 131.99, 33.21. ν_{max}/cm^{-1} (KBr disk) 3429 (vs, OH), 2954 (vw, CH), 2922 (vw, CH), 2900 (vw, CH), 1631 (w, C=O), 1598 (m, COOH), 1551 (w, CH_2), 1404 (w, CH_2), 1378 (w, Si-C), 1261 (vw), 1112 (s, Si-O), 1045 (w), 874 (w, SiC), 841 (w, CH), 751 (w, CH), 699 (w), 661 (w), 637 (w), 465 (s, SiO). CHN Microanalysis: Calculated 50.93 % C, 5.83 % H; Found 12.91 % C, 0.94 % H.

Potassium permanganate oxidation of 1,3,5,7,9,11,13,15-Octakis{2-[3-formylphenyldimethylsilyl] ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (17). Potassium permanganate (1.991 g. 12.60 mmol) in acetone (40 cm^3) was added drop-wise to a solution of **15** (3.090 g, 1.58 mmol) in acetone (10 cm^3). During the addition, an exotherm was observed. Once all the permanganate had been added, the solution was stirred for a further 2 hours and the solvent was removed by heating under reduced pressure. The resultant solid was extracted using hot methanol (4 × 100 cm^3) which was then removed under reduced pressure to leave a mixture of products (0.49 g). ^{1}H NMR (CD_3OD) δ 8.73 (s, C**H**), 8.42 (m, C**H**), 8.36 (broad s, C**H**), 8.12 (m, C**H**), 7.9-7.23 (m), 3.52 (m), 2.31 (m). ^{13}C NMR (CD_3OD) δ 177.21 (**C**OOH), 136.66, 131.99, 33.99. ν_{max}/cm^{-1} (KBr disk) 3429 (vs, OH), 2954 (vw, CH), 2922 (vw, CH), 2900 (vw, CH), 1631 (w, C=O), 1598 (m, COOH), 1551 (w, CH_2), 1404 (w, CH_2), 1378 (w, Si-C), 1261 (vw), 1112 (s, Si-O), 1045 (w), 874 (w, Si-C), 841 (w, CH), 751 (w, CH), 699 (w), 661 (w), 637 (w), 465 (s, Si-O).

Preparation of 1,3,5,7,9,11,13,15-Octakis{2-[4-carboxyphenyldimethylsilyl]ethyl}pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (18). 14 (0.301 g, 0.15 mmol) was placed in a sample vile and a layer of tissue was placed over the vial mouth to prevent the ingress of dust. After 4 months the sample was dried under reduced pressure (4 hours, 60 °C, 0.2 mmHg) to give >99 % conversion of the aldehyde groups to carboxylic acid groups (0.30 g, 97 % yield). Dec ~170 °C. ^{1}H NMR (CD_3OD) δ (s, C**H**O), 7.70 (d, J_{HH}=8.7 Hz, C**H**, 16H), 7.69 (d, J_{HH}=8.6 Hz, C**H**, 16H), 0.94 (broad s, C**H**$_2$, 16H), 0.70 (broad s, C**H**$_2$, 16H), 0.38 (s, Si-C**H**$_3$,



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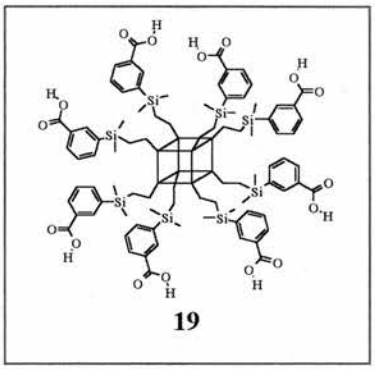
48H). ^{13}C NMR (CD_3OD) δ 172.1 (**C**OOH), 137.10 and 136.25 (Si-**C** and **C**-COOH), 131.93 (**C**H), 128.55 (**C**H), 10.31 (-**C**H_2-), 6.25 (-**C**H_2-), -1.88 (Si-**C**H_3). ν_{max}/cm^{-1} (KBr disk) 3429 (vs, OH), 2954 (vw, CH), 2922 (vw, CH), 2900 (vw, CH), 1631 (w, C=O), 1598 (m, COOH), 1551 (w, CH_2), 1404 (w, CH_2), 1378 (w, Si-C), 1261 (vw, Si-CH_3), 1112 (s, SiO), 1045 (w), 874 (w, Si-CH_3), 841 (w, CH), 751 (w, CH), 699 (w), 661 (w), 637 (w), 465 (s, SiO). CHN Microanalysis: Calculated (for pure acid) 50.93 % C, 5.83 % H; Found 52.49 % C, 5.72 % H.

Attempted preparation of 1,3,5,7,9,11,13,15-Octakis{2-[3-carboxyphenyldimethylsilyl]ethyl}-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (19). **15** (0.295 g, 0.14 mmol) was placed in a sample vile and a layer of tissue was placed over the vial mouth to prevent the ingress of dust. After 4 months the sample was dried under reduced pressure (4 hour, 60 °C, 0.2 mmHg) to yield a pale yellow crystalline material (0.30 g). ^{1}H NMR ($CDCl_3$) δ 10.02 (s, C**H**O, 3H), 9.1 (m, trace), 8.40 (m, trace), 7.97 broad s, C**H**, 8H), 7.81 (m, C**H**, 8H, 7.73-7.38 (m, C**H** and C**H**, 18H), 7.10 (m, trace), 4.06 (m, trace), 4.94 (m, trace), 4.06 (m, trace), 0.98 (m, -C**H**-, trace), 0.76 (broad s, C**H**$_2$, 16H), 0.52 (m, C**H**$_2$, 16H), -0.74 (broad s, Si-C**H**$_3$, 48H). ^{13}C NMR (CD_3OD) δ 171.9 (**C**OOH), 148.77, 141.80, 136.87 and 136.06 (Si-**C** and **C**-COOH), 135.47 (CH), 135.09 (CH), (**C**H), 128.57 (**C**H), 105.61, 54.12, 10.52 (-**C**H_2-), 7.34 (-**C**H_2-), 2.52, -1.92 (Si-**C**H_3). ν_{max}/cm^{-1} (KBr disk) 3402 (vs, OH), 2952 (vw, CH), 2900 (vw, CH), 1681 (w, CHO), 1599 (m, COOH), 1561 (w, CH), 1404 (w, CH), 1372 (w, Si-C), 1260 (vw), 1107 (s, SiO), 1043 (w), 874 (w, Si-CH_3), 842



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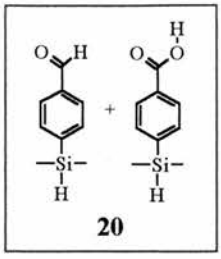
(w, CH), 695 (w), 661 (w), 552 (w), 462 (s, SiO). No satisfactory CHN microanalysis was obtained.

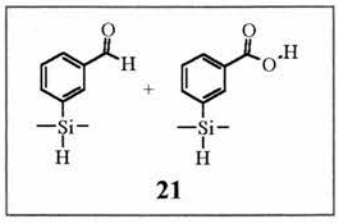
4-Dimethylsilanyl-benzaldehyde oxidation (20). 10 (0.698 g, 3.35 mmol), pyridinium p-toluenesulfonate (0.175 g, 0.69 mmol) and wet acetone (25 cm^3) were refluxed overnight. The solvent was removed under reduced pressure and diethyl ether (40 cm^3) was used to re-dissolve the residue. This solution was washed with sodium hydrogen carbonate solution (1M in water, 3 × 40 cm^3) followed by brine (40 cm^3) and the organic component was then dried over magnesium sulfate. After filtration, the solvent was removed under reduced pressure to give a colourless oil (0.40 g, 87 %). ^{1}H NMR ($CDCl_3$) 10.01 (s, C**H**O, 1H), 7.82 (d, J_{HH}=8.1 Hz, C**H**, 2H), 7.70 (d, J_{HH}=8.1 Hz, C**H**, 2H), 4.48 (sept, J_{HH}=3.7 Hz, Si-**H**, 1H), 0.37 (d, J_{HH}=3.8 Hz, Si-C**H**$_3$, 6H). ^{13}C NMR ($CDCl_3$) 192.64 (**C**HO), 146.12 and 136.77 (C-Si and **C**-CH), 134.57 (**C**-H), 128.72 (**C**-H), -3.98 (Si-**C**H_3).



20

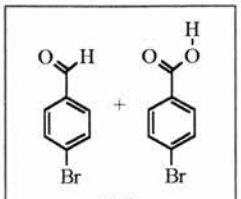
A portion of this material (0.103 g, 0.63 mmol) was placed in a vial and left exposed to air for 10 days. ^{1}H NMR ($CDCl_3$) (Integrations normalised against Si-H) δ 10.06 (s, C**H**O, 0.47H), 8.09 (d, J_{HH}=8.3 Hz, C**H**, 1.06H, acid), 7.84 (d, J_{HH}=8.5 Hz, C**H**, 0.94H, aldehyde), 7.68 (m, C**H**, 2H, acid and aldehyde), 4.50 (m, Si-**H**, 1H), 0.36 (m, Si-C**H**$_3$, 6H, aldehyde and acid). ^{13}C NMR ($CDCl_3$) δ 192.65 (**C**HO), 171.86 (**C**OOH), 147.58 (**C**-C, acid), 146.16 and 136.76 (Si and **C**-CH, aldehyde), 134.58 (**C**H, aldehyde), 134.32 (**C**H, acid), 134.12 (**C**H, acid), 129.17 (**C**-H, acid), 128.75 (**C**-H, aldehyde), -3.97 (Si-**C**H_3, aldehyde), -4.01 (Si-**C**H_3, acid)

3-Dimethylsilanyl-benzaldehyde oxidation (21). **11** (0.512 g, 2.46 mmol), pyridinium p-toluenesulfonate (0.130 g, 0.51 mmol) and wet acetone (25 cm^3) were refluxed overnight. The solvent was removed under reduced pressure and diethyl ether (40 cm^3) was used to re-dissolve the residue. This solution was washed with sodium hydrogen carbonate solution (1M in water, 3 × 40 cm^3) followed by brine (40 cm^3) and the organic component was then dried over magnesium sulfate. After filtration, the solvent was removed under reduced pressure to give a colourless oil (0.27 g, 82 %). ^{1}H NMR ($CDCl_3$) δ 10.06 (s, CO**H**, 1H), 8.07 (s, C**H**, 1H), 7.88 (m, C**H**, 1H), 7.81 (m, C**H**, 1H), 7.54 (m, C**H**, 1H), 4.47 (sept, Si-**H**), 0.39 (d, J_{HH}=3.8 Hz, Si-C**H**$_3$). ^{13}C NMR ($CDCl_3$) δ 192.73 (**C**HO), 140.01 (**C**-H), 138.93 and 135.64 (**C**-Si and **C**-C), 135.40 (**C**-H), 130.49 (**C**-H), 128.49 (**C**-H), -3.89 (Si-**C**H_3).


21

A portion of this material (0.106 g, 0.65 mmol) was placed in a vial and left exposed to air for 10 days. ^{1}H NMR ($CDCl_3$) (Integrations normalised against Si-H) δ 10.06 (s, CO**H**, 0.58H), 7.91 (m, C**H**, 1H), 7.72 (m, C**H**, 1H), 4.47 (m, Si**H**, 1H), 0.47 (m, Si-C**H**$_3$, 2.52H, acid), 0.41 (d, J_{HH}=3.8 Hz, Si-C**H**$_3$, 3.48H, aldehyde). ^{13}C NMR ($CDCl_3$) δ 192.92 (**C**HO), 171.86 (**C**OOH), 139.99 (**C**H, aldehyde), 139.33 (**C**-C, acid), 139.23 (**C**H, acid), 138.91 and 135.68 (**C**-Si and **C**-C, aldehyde), 138.21 (**C**-Si, acid), 135.46 (**C**H, aldehyde), 137.42 (**C**H, acid), 131.13 (**C**H, acid), 130.52 (**C**H, aldehyde), 128.52 (**C**H, aldehyde), 128.01 (**C**H, acid), -3.85 (Si-**C**H_3, acid), -3.89 (Si-**C**H_3, aldehyde).

4-Bromobenzaldehyde oxidation (22). 4-bromobenzaldehyde (0.30 g, 1.74 mmol) was placed in a vial and left exposed to air for 10 days.

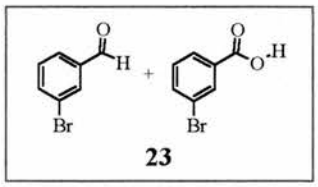


22

Before oxidation ^{1}H NMR ($CDCl_3$) δ 9.98, (s, C**H**O, 1H), 7.76 (d, J_{HH}=8.2 Hz, C**H**, 2H), 7.68 (d, J_{HH}=8.2 Hz, C**H**, 2H). ^{13}C NMR ($CDCl_3$) δ 191.06 (**C**HO), 135.09 (**C**H), 132.46 (**C**H), 130.98 (**C**H), 129.79 (**C**H).

After oxidation ^{1}H NMR ($CDCl_3$) δ 9.99, (s, C**H**O, 0.96H), 7.76 (m, C**H**, 2H, aldehyde and acid), 7.70 (m, C**H**, 2H, aldehyde and acid). ^{13}C NMR ($CDCl_3$) δ 191.06 (**C**HO), 135.09 (**C**H, aldehyde), 132.52 (**C**H, acid), 132.46 (**C**H, aldehyde), 131.05 (**C**H, acid),130.98 (**C**H, aldehyde), 129.82 (**C**H, acid), 129.79 (**C**H, aldehyde). Note: The fourth anticipated ^{13}C resonance from the benzoic acid component could not be detected against the background noise.

3-Bromobenzaldehyde oxidation (23). 3-bromobenzaldehyde (0.305 g, 1.76 mmol) was placed in a vial and left exposed to air for 10 days.



23

Before oxidation: ^{1}H NMR ($CDCl_3$) δ 9.99 (s, C**H**O, 1H), 8.07 (s, C**H**, 1H), 7.88 (m, C**H**, 1H), 7.81 (m, C**H**, 1H), 7.51 (m, C**H**, 1H). ^{13}C NMR ($CDCl_3$) δ 190.52 (**C**HO), 137.346 (**C**H), 133.43 (**C**H), 132.41 (**C**H), 131.15 (**C**H), 128.40 (**C**H), 123.40 (**C**H).

After oxidation: ^{1}H NMR ($CDCl_3$) δ 9.99 (s, C**H**O, 0.20H), [{8.27 (broad s, C**H**, acid), 8.07 (m, C**H**, aldehyde and acid), 7.80 (m, C**H**, aldehyde and acid), 7.40 (m,

C**H**, aldehyde and acid)}, 4H]. ^{13}C NMR ($CDCl_3$) δ 190.52 (**C**HO), 170.91 (**C**OOH), 137.346 (**C**H, aldehyde), 136.86 (**C**H, acid), 133.43 (**C**H, aldehyde), 133.22 (**C**H, acid), 132.41 (**C**H, aldehyde), 131.15 (**C**H, aldehyde), 130.11 (**C**H, acid), 128.80 (**C**H, acid), 128.40 (**C**H, aldehyde), 123.40 (**C**H, aldehyde), 122.61 (**C**H, acid).

2.5 Hydrolysable Precursors for Aldehyde functionalised POSS

Introduction

The carboxylic acid bearing POSS prepared in **Section 2.4** satisfy some of the aims of the project in that they are highly functionalised and have groups that may allow them to be linked together. There is however, an ethyl linkage between the POSS core and the aromatic ring system which may restrict the degree of order that will be possible in materials prepared from these molecules.

The relative ease with which the silane precursors for the POSS discussed in **Section 2.4** can be prepared suggested that a similar approach could be employed to prepare dioxolane bearing trichloro- and trialkoxysilanes that would be suitable for hydrolytic condensation reactions. Once de-protected and oxidised to their carboxylic acid form, POSS molecules prepared from this type of precursor would have the rigid structures desirable in molecular building blocks for the preparation of well-ordered materials.

The preparation of trifunctional silanes with aromatic components has been well documented (**Section 1.4**) and several approaches derived from previous studies were investigated here. Initially, attempts were made to react tetrachlorosilane with Grignard reagents and lithiated species formed from 3- and 4-bromophenyldioxolane (**8** and **9**) to prepare trichlorosilanes but unexpected side reactions rendered this approach ineffective. Experiments were then performed using ethoxysilanes in place of the tetrachlorosilane in an attempt to prepare trialkoxylsilanes. Alkoxysilanes are less reactive than their chlorosilane counterparts making them more stable and less prone to the side reactions that were observed during the experiments involving tetrachlorosilane. Despite being less reactive, alkoxysilanes can still be hydrolysed to silanols and hydrolytically condensed or, alternatively, can be converted to trichlorosilanes to render them more reactive.

Results and Discussion

Attempts to react metallated phenyldioxolanes with tetrachlorosilane resulted in the formation of rubbery polymeric solids and liquids which appear to be contain dioxolane fragments. The initial experiments were performed in a manner very similar to that described in **Section 2.4** for the preparation of dimethylsilylphenyldioxolanes. A Grignard reagent was prepared from **8** and then added to a ten-fold excess of tetrachlorosilane (***Figure 2.12***). As the silane had four possible reaction sites it was recognised that mixed products would be produced in the reaction. By using a large excess of the chlorosilane, it was expected that high yields of the mono-substituted species would be produced and this would be separated from the di-, tri- and tetra-

substituted species. However, within an hour of adding the Grignard reagent to the silane solution an insoluble solid gel formed. Sub-samples taken prior to complete gelation indicated that fragmentation of the dioxolane group was occurring during or after the reaction between the Grignard reagent and the tetrachlorosilane.

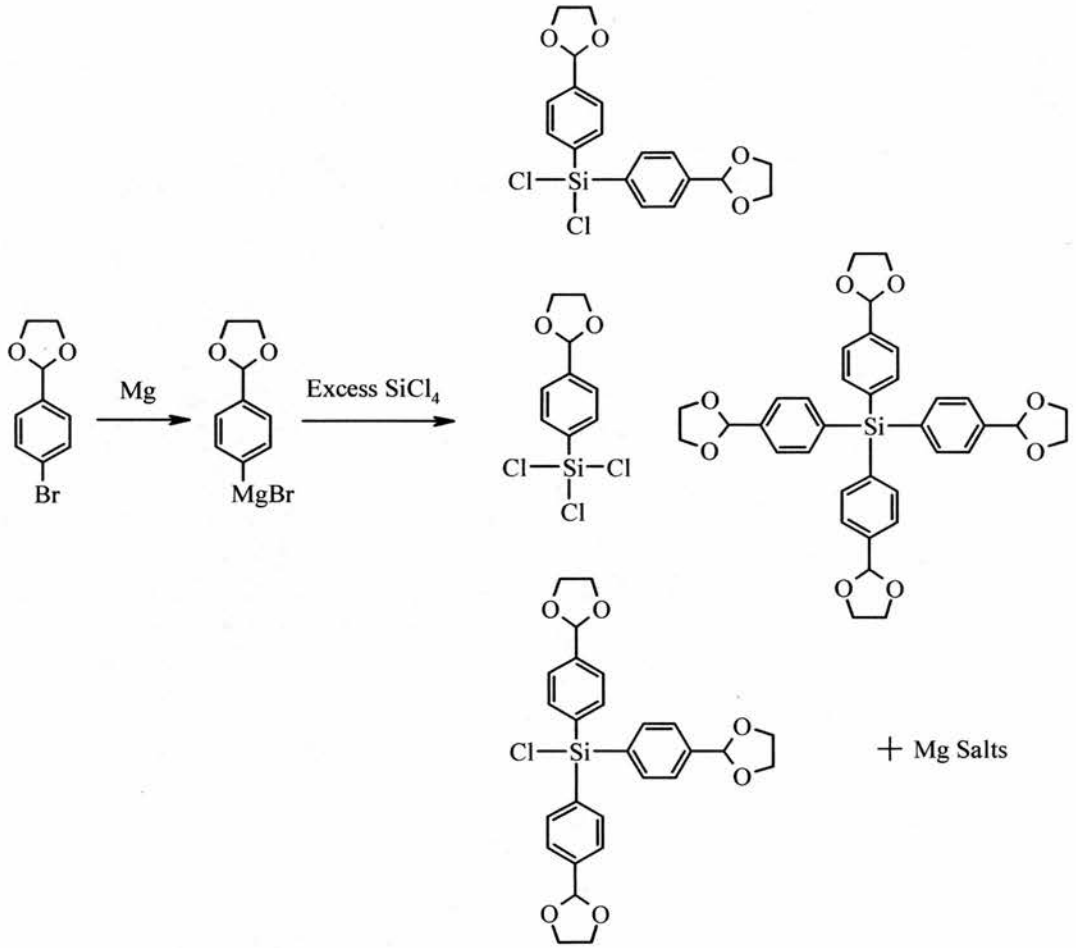


Figure 2.12. *Scheme for proposed reaction between a metallated dioxolane with tetrachlorosilane to produce a mixture of silanes dominated by the trichloro form. It should be noted that attempts to implement this scheme produced a gel rather than discrete silanes and is not therefore an accurate reflection of the reactions which actually occur under the conditions employed during this study.*

Repeating the experiment using **9** in place of **8** produced identical results and the synthetic methodology was changed slightly. The THF solvent was replaced with diethyl ether and the experiments were repeated but again, the brown polymeric material formed after addition of the Grignard to the silane solution. Anecdotal evidence suggested that by using a lithium reagent rather than a Grignard reagent, better results could be obtained [35] but experiments using lithiated phenyldioxolanes also produced the polymeric gel.

As the only difference between these experiments and those discussed in **Section 2.4** is the chlorosilane type, it can be assumed that the tetrachlorosilane is responsible for the formation of the polymer. It is feasible that the addition of the chlorosilane to the aromatic ring results in an inductive effect which destabilises the dioxolane group, either fragmenting it or rendering it susceptible to attack by the free chlorosilane, chlorosilane groups bound to the aromatic ring of the dioxolanes or by the metallated species. It is conceivable that the fragmentation of the dioxolane group is due to catalytic de-protection caused by traces of acid being present in the reaction mixture, but it would be expected that if this was the case, this type of cleavage would be observed in the reactions with dimethyl chlorosilane. Although cleavage of the dioxolane group does occur in the reactions involving dimethyl chlorosilane, it only occurs on a small scale. This suggests that addition of the dioxolane to tetrachlorosilane either weakens the dioxolane group or activates the trichlrosilane group in such a way as to allow it to break open the dioxolane ring.

To determine if the addition of the silane did destabilise the dioxolane group, attempts were made to react the Grignard reagent with tetraethoxysilane as this silane

was less reactive than tetrachlorosilane and was expected to exert less of an inductive effect. No discernible reaction was observed when the reactants were combined in the manner employed in the earlier experiments. Similar results were observed by Whittingham and Jarvie[36] and they overcame this problem by performing an *in situ* reaction where all the elements of the reaction mixture were placed in a flask and the solvent was added drop-wise until a critical concentration was achieved and reaction began. An attempt was made to use this approach but again, no reaction was observed. Whittingham and Jarvie were investigating reactions with fluoronated aromatics and it may be the case that these functional groups promoted the reaction through inductive effects on the system while the dioxolane species studied here may not exhibit the same behaviour.

The lack of reaction between the Grignard reagents and tetraethoxysilane was capitalised upon in work that was undertaken in collaboration with Michael Moffet as part of his senior honours research project.[37] Triethoxychlorosilane was reacted with Grignard reagents to produce what appear to be triethoxysilanes bearing dioxolane and aldehyde groups (***Figure 2.13.***). Due to the reactive nature of the chloro component of the silane and relatively unreactive nature of the ethoxy component, reaction occurs only with the chloro group. Satisfactory CHN microanalysis results were not obtained for the samples preventing full characterisation, but NMR, IR and GC-MS data (the IR and GC-MS data were collected by M. Moffet) all point towards the formation of this material. Time did not allow for detailed analysis of the compound and no pure samples were obtained.

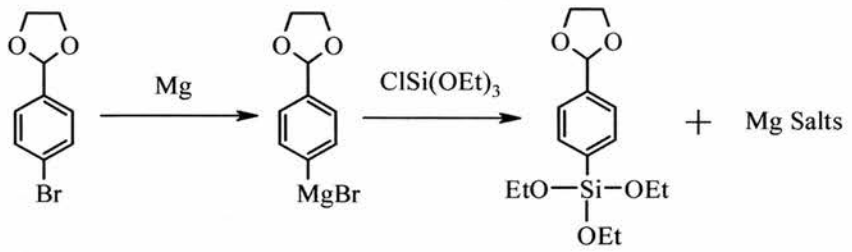


***Figure 2.13**. Scheme for proposed reaction between metallated bromodioxolanes and triethoxychlorosilane.*

Fractional distillation was employed in attempts to purify the product as it appeared to offer a simple means by which this could be achieved. Pure product was not recovered and it is suspected that the application of this technique was in fact counter productive. The earlier experiments suggested that trichlorosilanes of this type are unstable and although the triethoxy form may be more stable, the act of heating the molecule may promote a similar process to that observed during the earlier experiments. In this case, the presence of ethoxy groups rather than chloro groups may prevent the preparation of polymeric materials. Further attempts to purify this material should therefore be focused around the use of column chromatography.

Conclusions

It was not possible to follow up the promising results observed for the reaction between triethoxychlrorosilane and the Grignard reagent derived from **9** during this project but it appears that precursors suitable for the preparation of benzaldehyde POSS can be synthesised (***Figure 2.14***). Isolation of the aldehyde and dioxolane

components of **27** should be undertaken as a priority to allow confirmation of composition by microanalysis and investigation of the viability of POSS formation from either molecule.

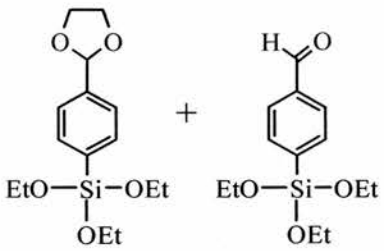


Figure 2.14. *The principle constituents of the product mixture from the reaction between triethoxychlorosilane and a Grignard reagent derived from 2-(3-bromo-phenyl)-[1,3]dioxolane (**27**).*

Although in the triethoxysilane forms, it should be possible to hydrolyse the ethoxy groups of the aldehyde and dioxolanes in product mixture **27** and perform hydrolytic condensations. Although it has been suggested that the components of **27** require separation, with the removal of contaminants, it may be possible to perform hydrolytic condensations on a mixture of aldehyde and dioxolane to yield POSS which can be fully de-protected to give aldehyde functionalised molecules.

If these molecules do not lend themselves to this type of reaction, it may be possible to convert them to trichlorsilanes which would be readily hydrolysed but these derivatives may not be stable. The results of these experiments suggest that the addition of a trichlorosilane group to **8** and **9** through reaction with tetrachlorsilane destabilises the dioxolane group or even promotes attack at this group by active species within the reaction mixture.

From the experiments described in **Section 2.4** it is clear that the oxidation rate of benzaldehyde functionalised POSS will be dependent on the isomer and it is likely that the 3-isomer will oxidise very rapidly in air. This would make the preparation of a carboxylic acid functionalised species a very simple matter. As in the case of 4-bromobenzaldehyde however, the 4-isomer of this POSS would be expected to oxidise much more slowly when exposed to atmospheric oxygen. With only one synthetic step being required to convert an aldehyde group to a carboxylic acid, alternatives to atmospheric oxidation should make oxidation if the 4-isomer a simple matter.

Experimental

General. Tetra-chlorosilane (Fluka), Tetra-ethoxysilane (Aldrich) were used without further purification as were magnesium turnings (Lancaster) and iodine (Fisher). Diethyl ether (BDH) was distilled from sodium under nitrogen. THF (BDH) was distilled from benzopheonone under nitrogen. Information on the analytical equipment and techniques is provided in **Appendix B**.

Preparation of 2-(4-Bromo-phenyl)-[1,3]dioxolane (8). Prepared as in **Section 2.4** (page 95).

Preparation of 2-(3-Bromo-phenyl)-[1,3]dioxolane (9). Prepared as in **Section 2.4** (page 96).

Reaction of tetrachlorosilane and a Grignard reagent prepared from 8 (24). A Grignard reagent was prepared from **8** (3.002 g, 13.11 mmol) as in **Section 2.4** and added *via* a canula to a solution of tetra-chlorosilane (22.605 g, 133.02 mmol) dissolved in dry THF (200 cm^3) under argon. This resulted in an exothermic reaction and a yellow solution being formed. After stirring for several hours the solution was transferred to another flask *via* a canula fitted with a glass wool filter to prevent the salt precipitate from being transferred. The excess tetra-chlorosilane was removed from the solution to leave the product mixture which thickened and solidified to a brown rubbery gel within the space of 2 hours.

In a repeat of this reaction a portion of the product mixture was removed and submitted to rapid short path distillation (65-89 °C, 0.3 mmHg) before gelation was complete. A small quantity of clear oil was recovered from the reaction mixture (0.62 g). ^{1}H NMR ($CDCl_3$) δ 7.23-8.11 (m [low intensity], C**H**), 4.01-4.34 (m, 0-C**H**$_2$-C**H**$_2$-O), 3.44-3.58 (m, O**H**), 1.83-2.10 (m).

In a subsequent experiment, stoichiometric quantities of the reactants were used but this also produced a brown rubbery material.

Reaction of tetrachlorosilane and a Grignard reagent prepared from 9 (25). A Grignard reagent was prepared from **9** (2.998 g, 13.09 mmol) as in **Section 2.4** and added *via* a canula to a solution of tetra-chlorosilane (22.286 g, 131.14 mmol) dissolved in dry THF (200 cm^3) under argon. This resulted in an exothermic reaction and a yellow solution being formed. After stirring for several hours the solution was

transferred to another flask *via* a canula fitted with a glass wool filter to prevent the salt precipitate from being transferred. The excess tetra-chlorosilane was removed from the solution to leave the product mixture which thickened and solidified to a brown rubbery gel within the space of 2 hours.

In a repeat of this reaction a portion of the product mixture was removed and submitted to rapid short path distillation (61-88 °C, 0.2 mmHg) before gelation was complete. A small quantity of clear oil was recovered from the reaction mixture (0.32 g). ^{1}H NMR ($CDCl_3$) δ 7.31-8.53 (m [low intensity], C**H**), 4.07-4.37 (m, 0-C**H**$_2$-C**H**$_2$-O), 3.43-3.72 (m, O**H**), 1.85-2.11 (m).

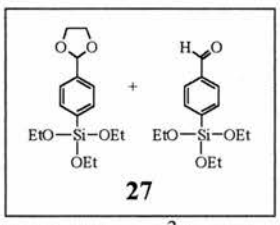
Further reactions were performed with diethyl ether as the solvent and various concentrations of the reaction mixtures, all with the same outcome.

Attempted *in situ* Grignard preparation to combine 8 and 9 with tetraethoxysilane. **8** (4.575 g, 19.97 mmol) and tetraethoxysilane were added to magnesium turnings (0.550 g, 22.92 mmol) under an argon atmosphere. Dry diethyl ether was then added drop-wise *via* the dropping funnel while the contents of the flask were stirred thoroughly. No reaction was observed. The experiment was repeated with a single crystal of iodine being added to the dry components but no reaction was observed even on heating the mixture.

This experiment was repeated using **9** in place of the **8**. Again, no reaction was observed.

Reaction of lithiated 8 with tetrachlorosilane (26). A solution of **8** (2.999 g, 13.12 mmol) in THF (50 cm^3) under an argon atmosphere was cooled in an acetone/dry-ice bath. n-Butyllithium in hexanes (2.5 M, 11 cm^3, 27.5 mmol) was added to the reaction mixture producing a golden solution which was stirred for 1 hour at –78 °C. This solution was then added to tetrachlorosilane (22.33 g, 131.47 mmol) in THF (50 cm^3) which had also been cooled to –78 °C. Once this solution had come to room temperature the excess tetra-chlorosilane was removed to produce the brown gel observed previously.

Grignard reagent and triethoxychlorosilane (27). A Grignard reagent was prepared from **8** (3.000 g, 13.1 mmol) as in **Section 2.4** and added *via* a canula to a solution of triethoxychlorosilane (2.784 g, 13.37 mmol) dissolved in dry THF (50 cm^3) under argon. The resultant solution was stirred overnight and the product recovered as a clear, colourless oil (1.13 g) by fractional distillation under reduced pressure (96 °C, 0.2 mm Hg). ^{1}H NMR ($CDCl_3$) δ 10.01 (s, C**H**O, 1H), 8.41 (m, C**H**, 1H, aldehyde), 8.21 (m, C**H**, 1H, aldehyde), 8.13 (m, C**H**, 1H, dioxolane), 8.00 (m, C**H**, 1H, aldehyde), 7.95 (m, C**H**, 1H, dioxolane), 7.78 (s, C**H**, 1H, aldehyde), 7.66 (m, C**H**, 1H, dioxolane), 7.45 (m), 5.83 (s, O-C**H**-O, 1H), 4.60 (m), 4.13 (m, O-C**H**$_2$-C**H**$_2$-O, 4H), 3.94 (m, O-C**H**$_2$-CH_3, 6H, aldehyde), 3.90 (m, O-C**H**$_2$-CH_3, 6H, dioxolane), 3.86 (m), 3.58 (m), 1.34 (overlapping m, O-CH_2-C**H**$_3$, 9H and 9H, aldehyde and dioxolane), 1.29 (m). Note: the ratio of aldehyde to dioxolane silanes in the product mixture was approximately 1:2 by ^{1}H NMR. ^{13}C NMR ($CDCl_3$) δ 192.76 (**C**HO), 142.04 (**C**-H, aldehyde), 138.61 and 138.02 (Si-**C** and **C**-CH, dioxolane)139.88 and 137.07 (**C**-Si and **C**-C, aldehyde), 136.55 (**C**-H, aldehyde), 135.98 (**C**H, dioxolane),



27

133.28 (**C**-H, aldehyde), 133.01 (**C**H, dioxolane), 129.52 (**C**-H, aldehyde), 128.98 (**C**H, dioxolane), 128.21 (**C**H, dioxolane), 104.34 (O-**C**H-O), 65.86 (O-**C**H_2-**C**H_2-O), -3.01 (Si-**C**H_3, aldehyde), -2.87 (Si-**C**H_3, dioxolane).

2.6 General Conclusions

Preparing POSS functionalised with carboxylic acid groups is not a trivial matter. Several routes have been attempted to prepare this type of molecule, but only two of these currently show promise.

Cobalt $(acac)_2$ oxidation of tolyl POSS was not viable, probably due to the electron withdrawing effect of the silsesquioxane core deactivating the methyl group to the action of the catalyst. It may be possible to oxidise tolyl groups attached to POSS when there are several atoms between the ring and POSS core but cubes of this type would have to be developed as none have yet been reported.

The range of techniques available to hydrolyse the ester-functionalised POSS studied in this project was severely restricted due to the POSS core being susceptible to attack by basic media. Only acid hydrolysis could be used and none of the techniques employed produced any detectable carboxylic acid groups. Only one type of ester functionalised POSS was used in this project however, so it is by no means certain that this approach will not produce positive results in ester functionalised POSS with different leaving groups.

Aldehyde-functionalised POSS can be successfully prepared from bromobenzaldehydes and can be readily oxidised to carboxylic acid bearing POSS through exposure to atmospheric oxygen. As this reaction takes several months to complete it would be beneficial to find a gentle oxidation reaction which will accelerate this process. The reaction pathway leading to the formation of the acid is becoming better understood and it should now be possible to produce bulk quantities of carboxylic acid-functionalised POSS to allow studies to be made into self-assembling networks *via* hydrogen bonding and metal co-ordination.

Although trichlorosilanes have not been prepared from bromophenyldioxolanes, it appears that a triethoxysilane can be synthesised. The techniques employed to date appear to also de-protect some of the dioxolane groups resulting in the preparation of an aldehyde from of the silane as well. Satisfactory microanalysis data has yet to be obtained to confirm this, but preliminary analysis suggests that this is the case.[37] Efforts should now be made to purify this material to allow full characterisation of the product and allow hydrolytic condensations to be attempted.

2.7 Bibliography

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Chapter 3 Pyridine-Functionalised POSS

3.1 General Introduction

The preparation of pyridine-functionalised POSS is a very desirable goal as pyridine groups readily co-ordinate with metals and are often used in self-assembly systems.[1, 2, 3, 4] Two strategies were devised to produce pyridine bearing POSS: the reaction of lithiated pyridine species with chlorosilane-functionalised POSS and hydrosilylation of pyridine derivatives to appropriately functionalised POSS.

Lithiopyridine/chlorosilane reactions have been well documented [5, 6, 7, 8] and appeared to offer a ready solution to the problem of preparing pyridine-functionalised POSS. Although this type of reaction does not generally produce high yields, the chemistry of the reaction between the two active species is relatively simple, making this an appealing approach.

Hydrosilylation reactions using pyridine derivatives offered the possibility of very high yields under mild conditions but there were concerns that pyridine groups would deactivate the catalyst through co-ordination or that N-silylation side reactions would be catalysed.[9] To date, little information on this type of reaction has been published and the outcome of the proposed experiments was unclear but the dearth of reports on the subject suggested that this strategy was not promising.

Both approaches were investigated as each had strengths and weaknesses but both had the potential to produce pyridine-functionalised POSS capable of being used to prepare POSS networks.

3.2 Reaction of Lithiated Methylpyridine with Chlorosilane-Functionalised POSS

Introduction

Many examples of synthetic routes based on the metallation of pyridine and its derivatives have been reported.[5, 6, 7, 8, 10, 11] Lithiation in particular can be readily achieved with good selectivity and this approach was therefore employed in these experiments. The yield of this type of reaction depends greatly upon the intended site of metallation, the reaction conditions and the pyridine derivative being used.

Direct lithiation of pyridine itself is possible but the absence of a directing element produces a mixture of 2, 3 and 4-isomers.[10] In this study however, reaction mixtures containing a single pyridyl lithium isomer were required to produce silsesquioxanes with uniform functionalities. In order to achieve this, the pyridine species used in these experiments required a functional group capable of directing the reaction towards the formation of a mono-isomer metallated form.

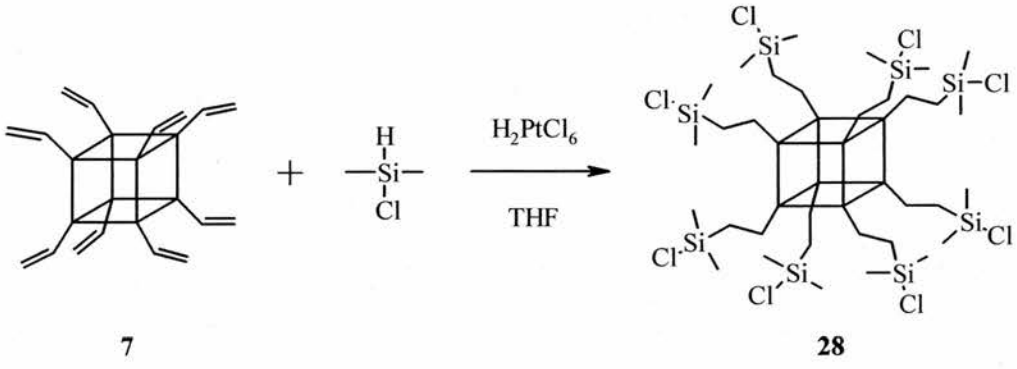
Bromopyridines undergo directed metallation with lithiation being favoured at the bromine position to produce 2, 3 and 4-pyridyl lithium depending on which

isomer is selected.[11, 12, 13, 14, 15] Once lithiation of the bromopyridine is achieved however, there are many possible side reactions that can occur leading to a variety of lithiated species being present in later synthetic steps.[16] These side reactions are difficult to suppress and although they can be accommodated in some experiments, they would be expected to produce silsesquioxanes with mixed functional groups in reactions with chlorosilane bearing POSS.

Methylpyridines can be selectively mono-lithated on their methyl groups through the removal of a proton, to produce a relatively stable metallated species. Several routes have been taken to achieve this particular metallation including reaction with potassamide, butyllithium, lithium di-isopropylamine and butyllithium in the presence of HMPA.[17, 18, 19, 20] The lithiation of all 3 isomers can be high yielding under suitable conditions and the resulting lithiated species are relatively stable if kept at low temperatures. Although there is still the possibility of side reactions after lithiation occurs, they can be more readily suppressed than those which occur during the lithiation of bromopyridines. This reduced potential for side reactions and selective lithiation made methylpyridines the obvious choice for the pyridyl component in these experiments.

The simplest chlorosilane-functionalised POSS that has been reported is $[SiO_{3/2}Cl]_8$ which has chlorine bound directly to the silicon atoms at the corner of the cube.[21] This could make an ideal reaction partner for lithiated pyridines as the pyridine groups would be held close to the POSS core, potentially making them excellent building blocks for extended porous networks. The preparation of this cube is potentially hazardous however, and the preliminary investigation into the

lithiopyridine/chlorosilane POSS reaction made use of $[SiO_{3/2}C_2H_4Si(CH_3)_2Cl]_8$ (**28**) instead (***Figure 3.1***).[22] This particular POSS is prepared through hydrosilylation of dimethylchlorosilane and octa-vinyl silsesquioxane **7** in THF using chloroplatinic acid as the catalyst. This solvent/catalyst combination promotes reaction at the α (terminal) carbon of the vinyl group, making it ideal for use in the preparation of molecular building blocks. If positive results were obtained from these experiments, further work using $[SiO_{3/2}Cl]_8$ would be undertaken in an effort to form pyridine bearing POSS with more rigid functional groups.



7 **28**

Figure 3.1. *The preparation of* $[SiO_{3/2}C_2H_4Si(CH_3)_2Cl]_8$ ***28.***

The reaction of methylpyridines with chlorosilanes *via* lithiated intermediates has been well documented which suggested that this approach to pyridine-functionalised POSS preparation would prove to be viable. In addition to discrete chlorosilanes, this approach has been successfully employed with polymers and dendrimers bearing multiple chlorosilane groups to produce pyridine-functionalised substrates.[8, 23] Good yields were reported for these experiments which suggested that this technique could be used with suitably functionalised POSS (***Figure 3.2***).

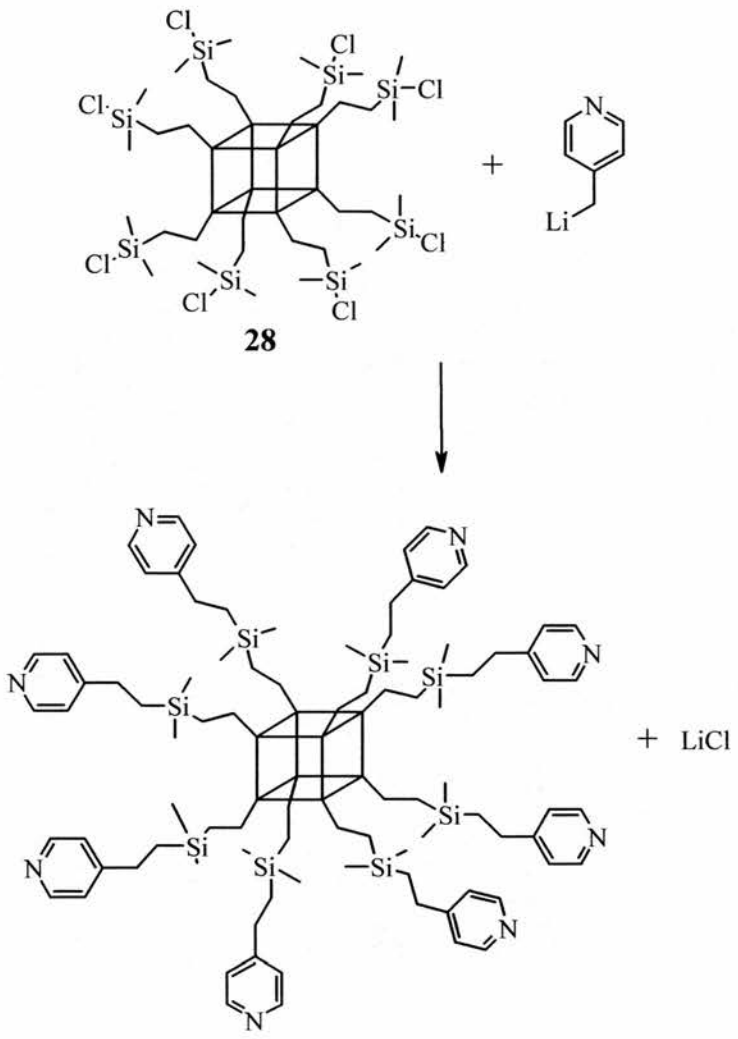


Figure 3.2. *Proposed reaction of 4-lithiomethylpyridine with* ***28***

A series of experiments were performed using all three methylpyridine isomers with a 10% excess and then a 100% excess of lithiated pyridyl species based on the quantity of butyllithium used. Although it was recognised that pyridine-functionalised POSS prepared from 2-methylpyridine would be very difficult to link together in extended networks, this species was used to allow comparisons to be made with the experiments performed by Cole-Hamilton *et al* using chlorosilane-functionalised co-polymers.[8, 23]

Results and Discussion

Both the FTIR and NMR data indicate that a portion of the reactants have combined in the expected manner in all of the experiments. The reactions involving the 2-isomer produced the best yields with the highest being in the region of 64 % while the highest yields obtained using 3- and 4-methylpyridine were approximately 23-26 % and 40 % respectively.

Although there were several unidentifiable resonances in the ^{1}H NMR data, the ethyl linkage established by the hydrosilylation reaction was readily identified and the integration of its peak area allowed normalisation of the other peak areas. Accurate yields could not be determined due to the nature of the products, but comparison of this peak area with those due to pyridyl groups allowed estimates to be made on the number of pyridyl groups bound to the POSS in the desired manner.

The comparatively low yield from the 3-methylpyridine reaction is in keeping with the unstable nature of this isomer on lithiation. Almost identical yields were obtained for the individual isomers when the quantity of lithiated material available for reaction was varied, indicating that the outcome of the reaction was not dependent on the availability of appropriately lithiated molecules.

Separation using TLC was unsuccessful despite a wide variety of solvents and solvent combinations being used. This could indicate that the distribution of functional groups across the POSS is close to being uniform but could also mean that the correct solvent combination had not been found.

Had attempts to produce **28** (see ***Figure 3.1***, page 127) resulted in the formation of a POSS which was not solely funtionalised with chlorosilane groups in the α position then results similar to those obtained from these experiments could be expected. This is very unlikely as NMR spectra from sub-samples of the POSS prior to reaction with the lithiated species indicated that almost pure mono-isomer **28** was used in all the experiments. It is possible that the chlorosilane groups underwent some form of reaction before they were exposed to the metallated species but in earlier experiments it was found that this molecule remained stable under a nitrogen atmosphere for over 24 hours. These observations suggest that the source of the undesired product groups is either by-products from the lithiation step or side reactions during the combination of the lithiated pyridine species and the chlorosilane-functionalised POSS.

It was suspected that the disappointing yields obtained from these experiments were due to a fundamental flaw in the experimental technique. Subsequent experiments investigating the preparation of pyridine derivatives for hydrosilylation to POSS took the same approach to lithiation but successfully produced a vinylsilane-functionalised pyridine from 4-methylpyridine however, with recovered yields of just over 40%. As the reaction producing a simple mono-silicon species has a similar yield to the reaction using the chlorosilane bearing POSS, it may be concluded that the low yield is associated with the behaviour of the lithio-pyridine species rather than the chlorosilane component.

It may be possible to use HMPA to stabilise the lithio-pyridine complex and increase the yield of the desired product by reducing the number of side reactions. HMPA has been used in conjunction with lithiated pyridines on numerous occasions and can stabilise this type of complex even at room temperature. On discussing the use of HMPA with the school safety officer however, it was decided that it would not be used on safety grounds.

Conclusions

Only a portion of the POSS-bound functional groups produced in these reactions were the expected ethyl-dimethyl-silyl-methyl-pyridine moieties with the remainder being by-products from the various synthetic steps. A solution containing a single, stable pyridyl lithium species would be expected to give close to 100% reaction with chlorosilane groups in the expected manner but, the results suggest that several lithiated species were present in the reaction mixtures, producing mixed products. The yields observed in these experiments may be acceptable when polymer catalyst supports such as those prepared by Cole-Hamilton *et al* are being prepared, but they are too low for the purposes of this project.

Had yields in the region of 80% or higher been obtained along with evidence of individual POSS reacting to differing extents it would be conceivable that a percentage of the POSS molecules would have reacted completely in the desired manner. It would then be expected that chromatography or even re-crystallisation could be used to isolate this material.

The lack of success using this route to pyridine bearing POSS was not entirely surprising as several steps are required to produce the two principle precursors, purification of these materials prior to the final reaction step is not practicable and the lithiated species is, by its very nature, very reactive. The presence of by-products is likely to provide many opportunities for further side reactions and the compounded effect of a series of reactions with yields below 100% would also be expected to lower the product yields.

The poor results obtained in these experiments suggested that the preparation of pyridine-functionalised POSS would be facilitated by the use of a simple synthetic route with as few synthetic steps as possible and for these steps to use only purified starting materials. Hydrosilylation reactions can satisfy both of these requirements and the next stage of the project was to attempt to use this type of reaction to produce POSS with higher numbers of pyridine functional groups.

Experimental

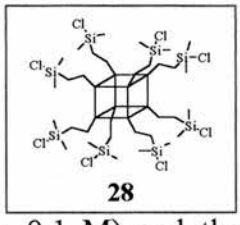
General. Chloroplatinic acid (Aldrich), dimethylchlorosilane (Lancaster), argon (BOC), nitrogen (BOC), ammonium chloride (Fisher), butyllithium (Lancaster), ethanol (Bamford Laboratories) were used as supplied. Di-isopropylamine (Lancaster) and all methylpyridine isomers (Aldrich) were purified by refluxing over sodium hydroxide (Fisher) and distillation onto Linde type 4A molecular sieves (Prolabo) under an argon atmosphere. Diethyl ether (BDH) and THF (Fisher) were distilled from sodium (Fisons) under nitrogen. Isopropanol (Fisher) was dried with calcium

hydride (Aldrich) and distilled on to Linde type 4A molecular sieves (Prolabo). Information on the analytical equipment and techniques is provided in **Appendix B**.

Preparation of 0.1 M chloroplatinic acid solution. Chloroplatinic acid (0.410g, 1.0 mmol) was placed in a 10 cm^3 volumetric flask under a constant flow of argon. The solution was made up with dry isopropanol, capped with an argon blanket and refrigerated for storage.

Preparation of $[SiO_{3/2}C_2H_3]_8$ (7). Prepared as in **Chapter 2** (page 94).

Preparation of $[SiO_{3/2}C_2H_4Si(CH_3)_2Cl]_8$ (28). Dry THF (50 cm^3) was added to **7** (0.500 g, 0.790 mmol) under an argon atmosphere. Dimethylchlorosilane (2.391 g, 25 mmol) was added to the solution followed by chloroplatinic acid in isopropanol (4 drops, 0.1 M) and the solution was stirred overnight. The solvent and excess silane were removed by rotary evaporation under reduced pressure and the sample was returned to atmospheric pressure under a nitrogen blanket. The off-white material obtained was re-dissolved in dry THF (20 cm^3) and the resultant solution was made ready for use by cooling with a dry-ice/acetone bath. ^1H NMR δ ($CDCl_3$) δ 0.84 (m, C**H**$_2$, 16H), 0.65 (m, C**H**$_2$, 16H), 0.41 (s, C**H**$_3$, 48H).



28

Preparation of lithium di-isopropylamine (LDA) solution. In a typical preparation, di-isopropylamine (0.710 g, 7.0 mmol) was added to dry THF (20 cm^3) under an argon atmosphere and the resultant solution was cooled using a dry-ice/acetone bath. Butyllithium (2.80 cm^3, 2.5 M in hexanes, 7.0 mmol) was slowly added and the

resultant solution was allowed to warm to 0 °C to ensure complete reaction before being cooled with a dry-ice/acetone bath prior to use.

Attempted preparation of $[SiO_{3/2}C_2H_4Si(CH_3)_2C_5H_4N]_8$ 3-isomer (10% excess) (29). 3-Methylpyridine (0.692 g, 7.430 mmol) was dissolved in THF (30 cm^3) under an argon atmosphere and cooled using a dry-ice/acetone bath. Cooled LDA solution (~7.0 mmol) was introduced drop-wise *via* a cannula while the reaction mixture was vigorously stirred producing a golden solution. After stirring for 1 hour a solution of **28** was added *via* a cannula, turning the solution yellow. The mixture was stirred for an additional 30 minutes before ethanol (1 cm^3) was added and the solution was allowed to come to room temperature. The volatile components of the reaction mixture were removed by rotary evaporation followed by short path distillation to leave a brown liquid residue which was passed rapidly through a 10 cm thick silica gel column (220-440 mesh, diethyl ether elutant). On removal of the solvent by evaporation a pale brown liquid was obtained (1.01 g). ^1H NMR ($CDCl_3$) δ 8.49 (m, C**H**, 1.8H), 8.40 (m, C**H**, 1.7H), 7.08 (m, C**H**, 1.8H), 7.00 (m, C**H**, 1.8H), 6.60 (broad s), 3.54 (m), 2.16 (m, C$\mathbf{H}_2$, 3.4H), 1.23 (m), 0.94 (broad m, C$\mathbf{H}_2$, 16H), 0.50 (broad m, C$\mathbf{H}_2$, 16H), {0.10 (broad set m, Si-C$\mathbf{H}_3$) and -0.03 (s, Si-C$\mathbf{H}_3$), 48H}.

This experiment was repeated with the solution being stirred for 3 hours after addition of the metallated species to the cooled solution of **28** before addition of the ethanol. This produced similar results to the previous experiment but additional by-products appeared to be generated by the extended reaction time.

Attempted preparation of $[SiO_{3/2}C_2H_4Si(CH_3)_2C_5H_4N]_8$ 3-isomer (100% excess) (30). 3-Methylpyridine (1.198 g, 12.86 mmol) was dissolved in THF (30 cm^3) under

an argon atmosphere and cooled using a dry-ice/acetone bath. Cooled LDA solution (~12.64 mmol) was introduced drop-wise *via* a cannula while the reaction mixture was vigorously stirred producing a golden solution. After stirring for 1 hour a solution of **28** was added *via* a cannula, turning the solution yellow. The mixture was stirred for a further 30 minutes before ethanol (2 cm^3) was added and the solution was allowed to come to room temperature. The volatile components of the reaction mixture were removed by rotary evaporation followed by short path distillation to leave a brown liquid residue which was passed rapidly through a 10 cm thick silica gel column (220-440 mesh, diethyl ether elutant). On removal of the solvent by evaporation a pale brown liquid was obtained (1.16 g). ^{1}H NMR ($CDCl_3$) δ 8.51 (m, C**H**, 1.6H), 8.39 (m, C**H**, 1.6H), 7.11 (m, C**H**, 1.6H), 7.00 (m, C**H**, 1.6H), 6.57 (broad s), 3.51 (m), 2.16 (m, C$\mathbf{H}_2$, 3.2H), 1.23 (m), 0.94 (broad m, C$\mathbf{H}_2$, 16H), 0.51 (broad m, C$\mathbf{H}_2$, 16H), {0.12 and (broad set m, Si-C$\mathbf{H}_3$) and -0.03 (s, Si-C$\mathbf{H}_3$), 48H}.

Attempted preparation of $[SiO_{3/2}C_2H_4Si(CH_3)_2C_5H_4N]_8$ 4-isomer (10% excess) (31). 4-Methylpyridine (0.689 g, 7.400mmol) was dissolved in THF (30 cm^3) under an argon atmosphere and cooled using a dry-ice/acetone bath. Cooled LDA solution (~7.0 mmol) was introduced drop-wise *via* a cannula while the reaction mixture was vigorously stirred producing a golden solution. After stirring for 1 hour a solution of **28** was added *via* a cannula, turning the solution yellow. The mixture was stirred for a further 30 minutes before ethanol (1 cm^3) was added and the solution was allowed to come to room temperature. The volatile components of the reaction mixture were removed by rotary evaporation followed by short path distillation to leave a brown liquid residue which was passed rapidly through a 10 cm thick silica gel column (220-440 mesh, diethyl ether elutant). On removal of the solvent by evaporation a pale

brown liquid was obtained (1.12 g). ^{1}H NMR ($CDCl_3$) δ 8.34 (broad s, C**H**, H), 6.90 (broad s, C**H**, 6.5H), 6.00 (broadened m), 2.11 (s, Si-C**H**$_2$-C, 6.5H), 1.11 and 1.02 (overlapping m, C**H**$_2$, 16H), 0.71 and 0.62 (overlapping m, C**H**$_2$, 16H), 0.11 (m, Si-C**H**$_3$, 48H). ^{13}C NMR ($CDCl_3$) δ 149.29 and 149.00 (CH and –CH_2-**C**-$(CH)_2$), 123.58 (**C**H), 25.35 (**C**H_2), 6.63 (**C**H_2), 6.14 (**C**H_2), 4.50 (**C**H_2), -2.57 (**C**H_2), -4.20 (Si-**C**H_3), -4.43 (Si-**C**H_3).

Attempted preparation of $[SiO_{3/2}C_2H_4Si(CH_3)_2C_5H_4N]_8$ 4-isomer (100% excess) (32). 4-Methylpyridine (1.224 g, 13.14 mmol) was dissolved in THF (30 cm^3) under an argon atmosphere and cooled using a dry-ice/acetone bath. Cooled LDA solution (~12.64 mmol) was introduced drop-wise *via* a cannula while the reaction mixture was vigorously stirred producing a golden solution. After stirring for 1 hour a solution of **28** was added *via* a cannula, turning the solution yellow. The mixture was stirred for a further 30 minutes before ethanol (1 cm^3) was added and the solution was allowed to come to room temperature. The volatile components of the reaction mixture were removed by rotary evaporation followed by short path distillation to leave a brown liquid residue which was passed rapidly through a 10 cm thick silica gel column (220-440 mesh, diethyl ether elutant). On removal of the solvent by evaporation a pale brown liquid was obtained (1.00 g). ^{1}H NMR ($CDCl_3$) δ 9.29 (broad s), 8.38 (broad s, C**H**, 6H), 6.92 (broad s, C**H**, 6H), 6.10 (broad s), 5.94 (m), 3.40 (broad s), 2.12 (s, Si-C**H**$_2$-C, 6H), 1.27 (m), 1.12 (broad m, C**H**$_2$, 16H), 0.68 (broad m, C**H**$_2$, 16H), 0.10 (broad m, Si-C**H**$_3$, 48H).

Attempted preparation of $[SiO_{3/2}C_2H_4Si(CH_3)_2C_5H_4N]_8$ 2-isomer (10% excess) (33). 2-Methylpyridine (0.693 g, 7.45 mmol) was dissolved in THF (30 cm^3) under an

argon atmosphere and cooled using a dry-ice/acetone bath. Cooled LDA solution (~7.40 mmol) was introduced drop-wise *via* a cannula while the reaction mixture was vigorously stirred producing a golden solution. After stirring for 1 hour a solution of **28** was added *via* a cannula, turning the solution brick red. The mixture was stirred for a further 30 minutes before ethanol (2 cm^3) was added and the solution was allowed to come to room temperature. The volatile components of the reaction mixture were removed by rotary evaporation followed by short path distillation to leave a brown liquid residue which was passed rapidly through a 10 cm thick silica gel column (220-440 mesh, diethyl ether elutant). On removal of the solvent by evaporation a pale brown liquid was obtained (1.00 g). ^{1}H NMR ($CDCl_3$) δ 8.56 (m, C**H**, 5.1H), 7.63 (m, C**H**, 5.2H), 7.18 (m, C**H**, 10.2H), 4.84 (s), 4.0 (m), 3.42 (m), 2.51-2.21 (m, possibly contains Si-C$\mathbf{H}_2$-C), 1.43 (s), 1.21 (m), 0.94 (broad m, C$\mathbf{H}_2$, 16H), 0.58 (broad m, possibly C$\mathbf{H}_2$, ~16H), 0.09 (overlapping m, Si-C$\mathbf{H}_3$ plus additional signals)

3.3 Preparation of Pyridine Derivatives for Hydrosilylation

Introduction

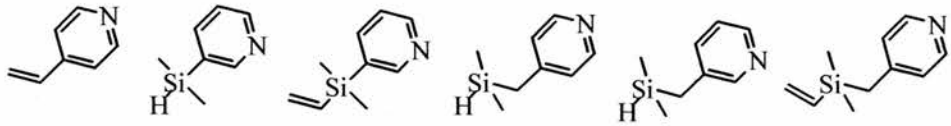
During the experimental phase of this project the only commercially available pyridine derivative that appeared suitable for use in hydrosilylation reactions was 4-vinylpyridine. To fully investigate the application of hydrosilylation in the creation of pyridine-functionalised POSS, it was determined that it would be necessary to prepare additional vinyl and silyl pyridines. As earlier experiments had demonstrated that

discrete silanes could be readily prepared through reactions between chlorosilanes and metallated species (**Chapter 2**), this approach was again employed. Attempts were made to modify 3-bromopyridine as well as 3- and 4-methyl pyridine *via* lithiation followed by reaction with dimethylchlorosilane and dimethylvinylchlorosilane.

3-Bromopyridine is readily lithiated at the bromine position,[7, 11, 12] but there are many opportunities for side reactions to occur once lithiation has been achieved and reaction conditions must be carefully controlled to keep these to a minimum.[16] Even when the conditions are strictly controlled, the recovered yields from reactions between chlorosilanes and the pyridyl-lithium formed are relatively low. Both 4- and 2-bromopyridine can also be lithiated and reacted with chlorosilanes, but the 3-isomer was selected for these experiments as it was more stable than the 4 and sterically superior to the 2. Several examples of silanes derived from 3-bromopyridine have been reported which indicated that this type of derivatisation was feasible.[13, 14, 15]

As has been discussed earlier in this chapter, lithiation of methylpyridines can be performed selectively on the methyl group.[17, 18, 19] A stable lithiated species can be prepared from 2-methylpyridine but POSS bearing functional groups derived from this molecule would be very difficult to link together due to steric hindrance and experiments were therefore only performed using the 3 and 4-isomers. As well as increasing the range of silanes available for hydrosilylation, preparing silanes from methylpyridines was expected produce molecules with different stabilities and reactivities to those of silanes derived from 3-bromopyridine.

Had all of the proposed reactions proved successful, a pool of derivatives would have been available for hydrosilylation offering the possibility of preparing POSS with various units between the cube and pyridine ring as well as different configurations for the groups interacting with the catalyst (***Figure 3.3***). Previous experiments indicated that the yields from these reactions would be low but fractional distillation offered a simple means by which the products could be obtained in a pure form.



34 **35** **36** **37** **38**

Figure 3.3*. The proposed range of pyridine derivatives suitable for hydrosilylation to POSS cube: (from left to right) 4-vinylpyridine, 3-(dimethyl-silanyl)-pyridine (**34**), 3-(dimethyl-vinyl-silanyl)-pyridine (**35**), 4-(dimethylsilanylmethyl)-pyridine (**36**), 3-(dimethylsilanylmethyl)-pyridine (**37**), 4-(dimethylvinylsilanyl)-pyridine (**38**).*

Results and Discussion

Throughout these experiments it was found that careful temperature control was the key to successful formation of the silicon bearing pyridines. Without the use of low temperatures during the reaction phase, side reactions were observed resulting in low product yields or polymerisation.

Pyridine derivatives **34**, **35** and **38** were prepared in relatively high yield. Derivative **34**, 3-dimethylsilylpyridine, had been prepared previously by Itami *et al*[6] but this was not known until after the material had been synthesised. Derivatives **35**, 3-vinyldimethylsilylpyridine, and **38**, 4-vinyldimethylsilylmethylpyridine, do appear to be new however. Although the method used to prepare derivative **34** was devised without knowledge of the work undertaken by Itami and co-workers, it was very similar to the approach taken by them. It took several attempts to prepare derivatives **35** and **38** as methods described elsewhere for similar reactions proved to be inadequate, producing either very low yields or none of the desired product.

The reaction of dimethylvinylchlorosilane with the lithiated forms of 3-bromopyridine and 4-methylpyridine proceeded as expected, but dimethylchlorosilane could only be combined satisfactorily with 3-lithiopyridine. No pure product was isolated from the reaction between dimethylchlorosilane and the lithiated form of 4-methylpyridine but NMR spectroscopy indicates that a quantity of the expected product has been prepared. Various molecules with similar compositions, possibly isomers, have also been formed and appear to dominate the product mixture. A number of resonances for Si-H groups are present in the ^{1}H NMR spectra suggesting that the by-products produced in these reactions are pyridines which have been metallated at several points resulting in individual molecules bearing multiple Si-H groups or a range of isomers with very similar properties.

Reducing the reaction temperature to –101 °C did not produce any discernible change in the outcome of the reaction suggesting that the problem was not due to unwanted lithiation of the pyridines prior to introduction of the silane as it would be

expected that this would be reduced at this lower temperature. As identical reaction conditions can be used to produce satisfactory yields of vinyldimethylsilylpyridines it is suspected that the side reactions are occurring during or after the addition of the dimethylchlorosilane.

The initial experiments into derivatising methylpyridine were performed with the 4-isomer as the lithiated intermediate formed from it was expected to be relatively stable. The 3-isomer is not as well stabilised when lithiated but to determine if the isomer used in the reaction affected the outcome, an attempt was made to lithiate it and react the metallated species with dimethylchlorosilane. The product mixture from this reaction bore a striking similarity to that obtained from the 4-isomer indicating that the isomer and stability of the intermediates does not affect the outcome of the reaction to any great extent.

All of the derivatives prepared are unstable and degrade at room temperature or in the presence of air. Mixed products are generated as the materials degrade but the exact nature of the degradation mechanism is difficult to determine as more than one process appears to occur. The improved stability of all the derivatives under an argon atmosphere suggests that oxidation is one of the likely causes of the degradation observed. The vinyl silanes are relatively stable and can be maintained for several weeks by refrigeration under an argon atmosphere but **34** degrades over several days under the same conditions. In addition to colour changes and the appearance of contaminants in samples of the compound, **34** underwent polymerisation with small particles forming over several weeks. Although there was sufficient polymeric

material for its presence to be observed, there was insufficient to make analysis practical.

No satisfactory microanalysis results could be obtained from any of the derivatives despite the NMR data and TLC indicating that the samples were effectively pure. The level of nitrogen measured in the samples was always excessively high but without accompanying high values for carbon which would have been associated with quantities of residual pyridine or extra pyridine units reacting. The microanalysis technician performing the analysis identified the problem as an artefact created by the analysis apparatus and high resolution mass spectrometry was therefore used to confirm the identification of the reaction products.[24]

Conclusions

Reacting lithiated pyridines with chlorosilanes has proved to be a viable route to prepare precursors which have the potential to be used in hydrosilylation reactions. The recovered yields are low for both the methylpyridine and bromopyridine derivatives, with the yield of **38** being is similar to that observed for the equivalent reaction between 4-methylpyridine and **28** in **Section 3.2**.

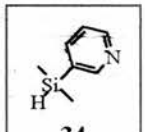
The silanes that were prepared are unstable with rapid degradation occurring if the samples are not placed under an argon blanket and refrigerated. This brings in to question the stability of any pyridine-functionalised POSS that may be prepared but their actual behaviour can only be speculated upon at this stage. It may be that these molecules will have to be kept under inert atmospheres to prevent oxidation but it is

anticipated that once incorporated into an extended structure they will be less prone to polymerisation.

Experimental

General. The starting materials and reagents used were prepared as in **Section 3.2** above. In addition, 3-bromopyridine (Aldrich), dimethylchlorosilane (Aldrich) and dimethylvinylsilane (Aldrich) were used as supplied. Information on the analytical equipment and techniques is provided in **Appendix B**.

Preparation of 3-(Dimethyl-silanyl)-pyridine (34). 6-Butyllithium (10 cm^3, 2.5 M in hexanes, 25.0 mmol) was added to dry diethyl ether (25 cm^3) under an argon atmosphere and cooled over a dry-ice/acetone bath.



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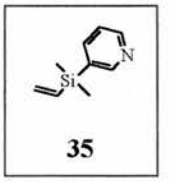
3-Bromopyridine (3.005 g, 19.0 mmol) dissolved in diethyl ether (20 cm^3) was then added *via* a pressure equalising dropping funnel over 20 minutes with vigorous stirring. The mixture was stirred for a further 20 minutes before dimethylchlorosilane (2.505 g, 26.5 mmol) dissolved in diethyl ether (5 cm^3) was added *via* a cannula from a schlenk tube cooled over a dry-ice/acetone bath. The yellow solution was allowed to come to room temperature slowly and then added to a saturated aqueous ammonium chloride solution (50 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined extracts were dried over magnesium sulphate, filtered and the solvent was removed by rotary evaporation. Distillation under reduced pressure (100 °C, 22 mmHg) produced a colourless air sensitive liquid (1.14 g, 44 %) which analysis confirmed as 3-(dimethyl-silanyl)-pyridine.[6] ^{1}H NMR ($CDCl_3$) δ 8.68 (s, C**H**, 1H), 8.58 (m, C**H**, 1H), 7.82 (m, C**H**, 1H), 7.23 (m, C**H**, 1H), 4.43 (sept, J_{HH}=3.8 Hz, Si**H**, 1H), 0.39 (s, C$\mathbf{H}_3$, 6H). ^{13}C NMR ($CDCl_3$) δ 154.35 (C-**C**-N), 150.24 (C-**C**-N),

141.74 (**C**-H), 132.36 (**C**-Si), 123.28 (**C**-H), -4.05 (Si-**C**H_3). ν_{max}/cm^{-1} (NaCl, no solvent) 2978 (w), 2956 (m), 2897 (m), 2859 (m), 2790 (w), 2106 (s, SiH), 1926 (w), 1914 (w), 1576 (s, aromatic C), 1556 (s, aromatic C), 1472 (m, aromatic C), 1392 (s, Si-C), 1328 (m), 1249 (s, Si-CH_3), 1212 (w), 1195 (m), 1123 (s), 1024 (broad s, SiH), 822 (s, SiH), 768 (s, CH), 712 (s), 695 (s), 626 (s), 611 (m), 526 (s). HRMS: Found 137.065; Calculated 137.066.

Preparation of 3-(dimethyl-vinyl-silanyl)pyridine (35). Butyllithium (10.8 cm^3, 2.5 M in hexanes, 27 mmol) was added to dry diethyl ether (25 cm^3) under an argon atmosphere and cooled over a dry-ice/acetone bath. 3-Bromopyridine (3.220 g, 20.4 mmol) dissolved in diethyl ether (20 cm^3) was then added *via* a pressure equalising dropping funnel over 20 minutes with vigorous stirring. The mixture was stirred for a further 20 minutes before dimethylvinylchlorosilane (3.403 g, 28.2mmol) dissolved in diethyl ether (5 cm^3) was added *via* a cannula from a schlenk tube cooled over a dry-ice/acetone bath. The yellow solution was allowed to come to room temperature slowly and then added to a saturated aqueous ammonium chloride solution (50 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined extracts were dried over magnesium sulphate, filtered and the solvent was removed by rotary evaporation. Distillation under reduced pressure (60 °C, 0.5 mmHg) produced a colourless air sensitive liquid (1.74 g, 52 %). ^1H NMR ($CDCl_3$) δ 8.69 (s, C**H**, 1H), 8.57 (m, C**H**, 1H), 7.79 (m, C**H**, 1H), 7.26 (m, C**H**, 1H), 5.72-6.30 (m, C**H**=CH_2), 0.33 (s, CH_3, 3H). ^{13}C NMR ($CDCl_3$) δ 154.27 (CN**C**), 150.04 (**C**NC), 141.52 (**C**H), 133.78 and 133.25 (**C**H and **C**=C), 136.678 (**C**=C), 123.19 (CH), -3.11 (Si-**C**H_3). ν_{max}/cm^{-1} (NaCl, no solvent) 3060 (m, C=C-H), 3021 (s, C=C-H), 2978 (m), 2956 (s), 2897 (m), 2859 (m), 2790 (w), 1926 (w), 1914



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(w), 1593 (m, C=C), 1576 (s, aromatic C), 1556 (s, aromatic C), 1472 (m, aromatic C), 1394 (s, C-Si), 1328 (m), 1248 (s, Si-CH_3), 1212 (w), 1195 (m), 1123 (s), 1006 (s, C=C), 952 (s, C=C), 822 (s, Si-CH_3), 768 (s, CH), 712 (s), 695 (s), 626 (s), 611 (m), 526 (s). HRMS: Found 163.081; Calculated 163.082.

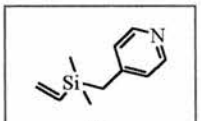
Preparation of lithium di-isopropylamine. LDA was prepared in the manner described earlier in this chapter (page 125) with quantities being varied to produce appropriate volumes of the solution suitable for the lithiation being attempted.

Attempted preparation of 4-(Dimethylsilanylmethyl)-pyridine (36). 4-Methylpyridine (6.701 g, 72.0 mmol) was dissolved in THF (25 cm^3) under an argon atmosphere and cooled using a dry-ice/acetone bath. LDA solution (~66.0 mmol), cooled using a dry-ice/acetone bath, was slowly added to the mixture which was then stirred for 30 minutes before a cooled solution of dimethylchlorosilane (6.794 g, 71.8 mmol) in THF (10 cm^3) was added. The resultant mixture was stirred and allowed to come to room temperature before being added to saturated aqueous ammonium chloride solution (50 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined extracts were dried over magnesium sulphate, filtered and the solvent was removed by evaporation. Distillation under reduced pressure (95 °C, 0.2 mmHg) produced a clear, air sensitive liquid (1.80 g). ^{1}H NMR ($CDCl_3$) δ 8.37 (m, C**H**), 6.92 (m, C**H**), 4.21 (m, Si**H**), 4.18 (m, Si**H**), 3.88 (sept, J_{HH}=3.2 Hz, Si**H**), 2.08 (m, C$\mathbf{H}_2$), 0.13 (m, SiC$\mathbf{H}_3$), 0.09 (m, SiC$\mathbf{H}_3$), 0.01 (m, SiC$\mathbf{H}_3$).

Attempted preparation of 3-Dimethylsilanylmethyl-pyridine (37). 3-Methylpyridine (5.588 g, 60.0 mmol) was dissolved in THF (40 cm^3) under an argon

atmosphere and cooled using a dry-ice/acetone bath. LDA solution (~55.0 mmol) cooled using a dry-ice/acetone bath was slowly added to the mixture which was then stirred for 30 minutes before a cooled solution of dimethylchlorosilane (5.832 g, 61.6 mmol) in THF (10 cm^3) was added. The resultant mixture was stirred and allowed to come to room temperature before being added to saturated aqueous ammonium chloride solution (50 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined extracts were dried over magnesium sulphate, filtered and the solvent was removed by evaporation. Distillation under reduced pressure (95 °C, 0.2 mmHg) produced a clear, air sensitive liquid (2.13g). ^{1}H NMR ($CDCl_3$) δ 8.35 (broad m, CH), 7.40 (m, C**H**), 7.15 (broad m, C**H**), 4.14 (m, Si**H**), 3.91 (m, Si**H**), 3.69 (m, Si**H**), 2.27 (broad s, C$\mathbf{H}_2$), 0.13 (m, C$\mathbf{H}_3$), 0.09 (m, C$\mathbf{H}_3$), 0.04 (m, C$\mathbf{H}_3$).

Preparation of 4-Dimethylvinylsilylmethylpyridine (38). 4-Methylpyridine (4.021 g, 37.4 mmol) was dissolved in THF (25 cm^3) under an argon atmosphere and cooled using a dry-ice/acetone bath.



38

LDA solution (~33.8 mmol) cooled using a dry-ice/acetone bath was slowly added to the mixture which was then stirred for 30 minutes before a cooled solution of dimethylvinylchlorosilane (4.100 g, 34.0 mmol) in THF (10 cm^3) was added. The resultant mixture was stirred and allowed to come to room temperature before being added to saturated aqueous ammonium chloride solution (50 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined extracts were dried over magnesium sulphate, filtered and the solvent was removed by evaporation. Distillation under reduced pressure (110 °C, 0.2 mmHg) produced a clear, air sensitive liquid (2.88 g, 43 % yield). ^{1}H NMR ($CDCl_3$) δ 8.41 (d, J_{HH}=8.5 Hz, C**H**, 2H), 6.89 (d, J_{HH}=8.5 Hz, C**H**, 2H), 6.18-5.61 (m, C**H**=C$\mathbf{H}_2$, 3H), 2.14 (s, C$\mathbf{H}_2$, 2H), 0.10 (s, C$\mathbf{H}_3$, 6H). ^{13}C

NMR ($CDCl_3$) δ 149.62 and 149.30 (**C**N**C** and **C**CH_2), 136.95 (**C**=C), 133.06 (**C**=C), 123.67 (**C**H), 26.19 (Si-**C**H_2-C), -3.84 (Si-**C**H_3). ν_{max}/cm^{-1} (NaCl, no solvent) 3096 (w), 3065 (s, C=C-H), 3050 (m), 3020 (s, C=C-H), 2985 (m), 2958 (s, CH), 2897 (m), 2805 (w), 2663 (vw), 2480 (w), 2358 (vw), 2302 (vw), 2278 (vw), 2216 (vw), 2024 (w), 1932 (w), 1913 (w), 1845 (vw), 1600 (vs, C=C), 1556 (s, aromatic C), 1493 (s, aromatic C), 1415 (vs), 1337 (w), 1250 (s, Si-CH_3), 1214 (s), 1151 (s), 1115 (m), 1067 (m), 1009 (s, C=C), 992 (s), 955 (s, C=C), 909 (m), 835 (vs, Si-CH_3), 785 (s, CH), 757 (s), 727 (m, CH), 694 (m), 667 (m), 644 (w), 595 (m), 563 (m), 515 (s). HRMS: Mass found 177.098; Calculated 177.097.

3.4 Hydrosilylation of Pyridine Derivatives to POSS Cubes

Introduction

Once a range of vinyl and silyl pyridine derivatives were available, attempts were made to hydrosilylate them to suitable silsesquioxane cubes. Literature reports of hydrosilylations involving pyridines are relatively rare but this type of reaction has been documented, indicating that it is possible.[7, 13, 25, 26] Although Yoshida *et al* used a rhodium catalyst to hydrosilylate dimethylsilylpyridines to olefins, it was decided to carry out a preliminary study using chloroplatinic acid and platinum (dvs) catalysts as these had been used throughout this project. Initially there were concerns that the pyridine derivatives could co-ordinate irreversibly with the metal component of the catalysts through their pyridine groups, but the study performed by Khonina *et al* using chloroplatinic acid and 4-vinylpyridine indicated that it was likely that this would not be the case.[27]

Previously reported POSS $[SiO_{3/2}H]_8$ (**2**), $[SiO_{3/2}C_2H_3]_8$ (**7**) and $[SiO_{3/2}C_2H_4Si(CH_3)_2H]_8$ (**39**)[27] were selected for reaction with the pyridine derivatives described in **Section 3.2**, giving a number of potential products **(Figures 3.4, 3.5, 3.6)**. By using both different POSS and pyridine derivatives, it was also hoped that if any problems were encountered in performing the planned reactions an insight might be gained into their cause.

These experiments were attempted towards the end of the project and were therefore only a preliminary study to investigate the viability of the technique. It was anticipated that any positive results would prompt further studies at a later date when a more detailed investigation could be undertaken.

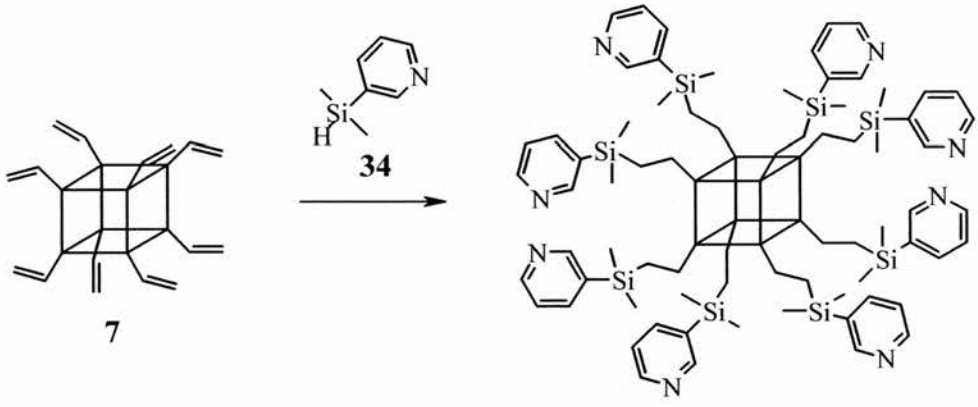


Figure 3.4. *Possible hydrosilylation reaction between POSS* ***7*** *and derivative* ***34****.*

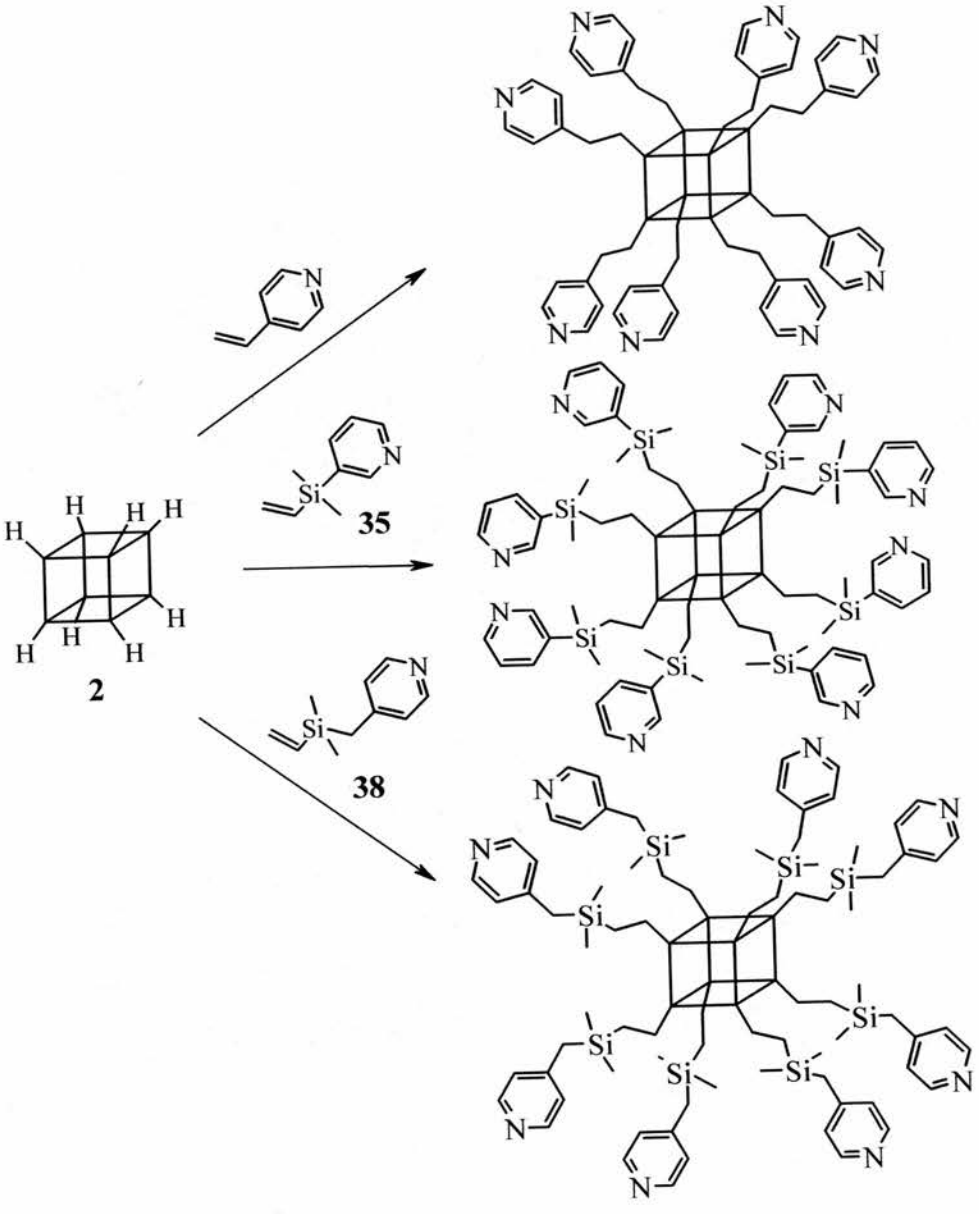


***Figure 3.5**. Possible products from hydrosilylation of derivatives 4-vinylpyridine, derivative **35** and derivative **38** with POSS **2**.*

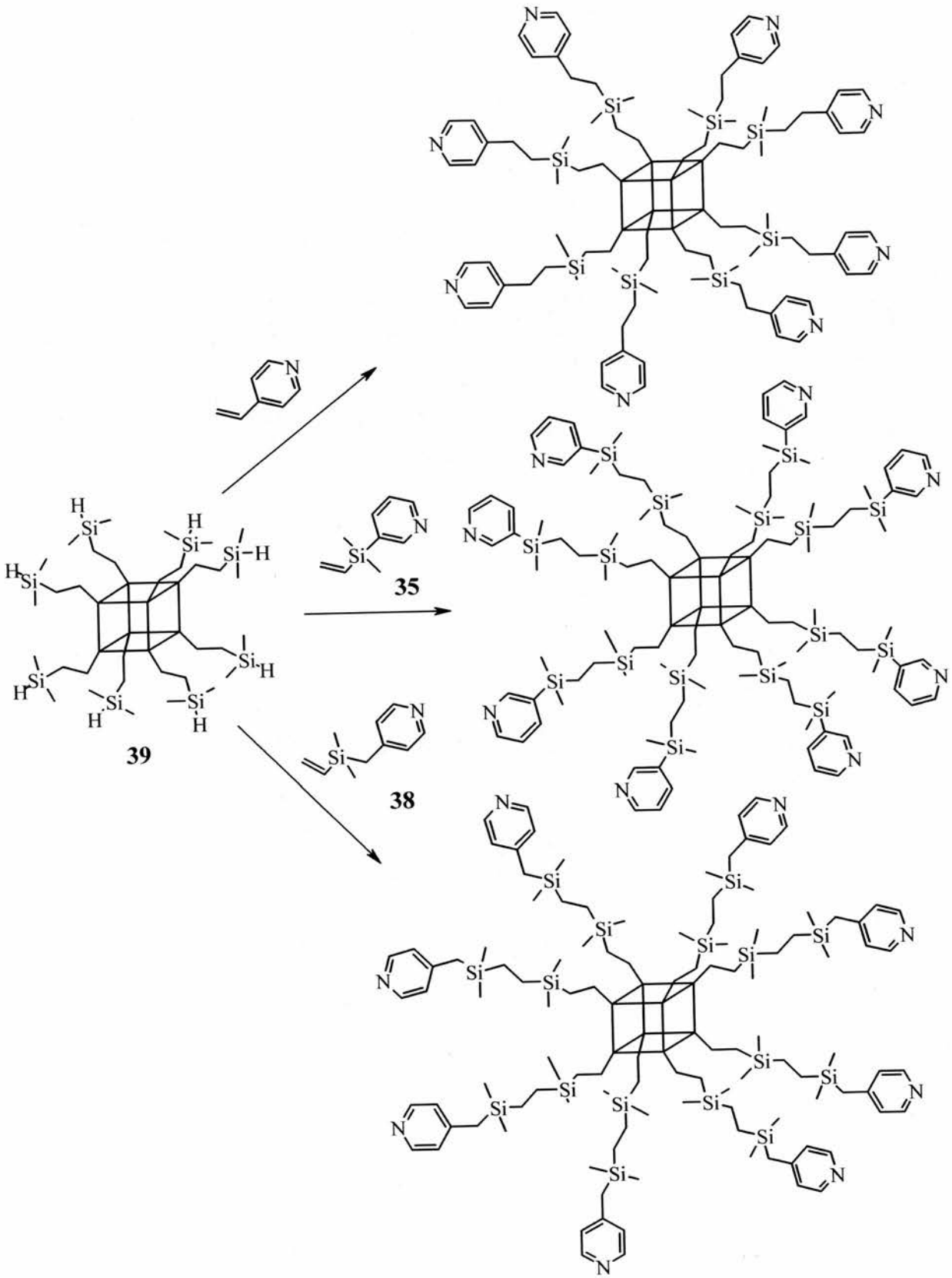
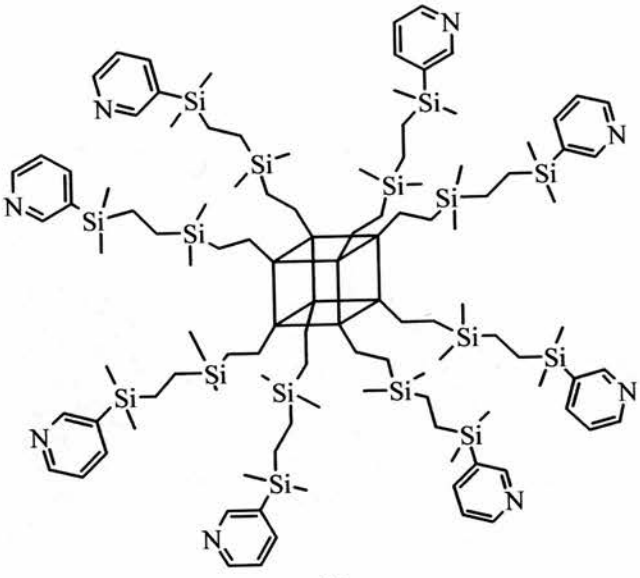


***Figure 3.6**. Possible products of hydrosilylation of POSS **39** with vinylpyridine, derivative **35** and derivative **38**.*

Results and Discussion

It was found that many of the POSS/pyridine derivative/catalyst combinations did not yield the anticipated hydrosilylated products. In some cases no reaction was observed, while in others, the pyridine derivative reacted with itself either spontaneously or, possibly, with the assistance of the hydrosilylation catalyst. Hydrosilylation appeared to be successful in two cases however and two new POSS, $[SiO_{3/2}C_2H_4Si(CH_3)_2C_2H_4Si(CH_3)_2C_5H_4N]_8$ (**44**) and $[SiO_{3/2}C_2H_4Si(CH_3)_2C_2H_4Si(CH_3)_2CH_2C_5H_4N]_8$ (**45**) (***Figure 3.7***) appear to have been prepared although the exact nature of the reaction products cannot be confirmed at present.

Attempting to hydrosilylate octa-vinyl POSS **7** with silyl derivative **34** using both chloroplatinic acid and platinum (dvs) produces polymeric gels which form rubbery polymers when dried. Analysis of these materials using FTIR suggests that they may be generated by N-silylation of **34** as the vinyl groups of the POSS remain intact in the polymer while the number of Si-H groups is reduced. Yoshida *et al* successfully hydrosilylated **34** to several different vinyl bearing substrates using a rhodium catalyst, demonstrating that the molecule can be used in this type of reaction. This suggests that the platinum catalysts employed here are not appropriate for use with pyridine derivatives bearing Si-H moieties.



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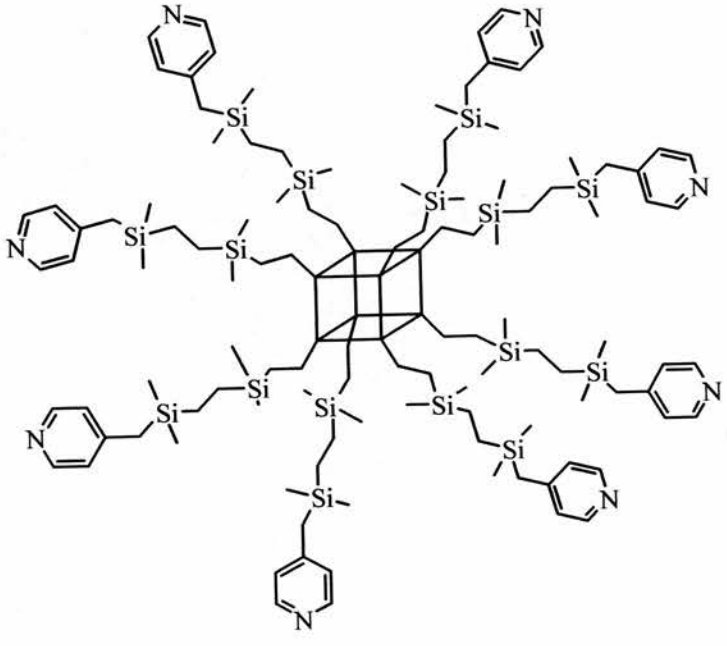


45

Figure 3.7. $[SiO_{3/2}C_2H_4Si(CH_3)_2C_2H_4Si(CH_3)_2C_5H_4N]_8$ ***(44)*** *and*

$[SiO_{3/2}C_2H_4Si(CH_3)_2C_2H_4\,Si(CH_3)_2CH_2C_5H_4N]_8$ ***(45)***

Only one silyl pyridine derivative was successfully prepared in **Section 3.2** which prevented comparative experiments being attempted in an effort to determine why the polymeric material is formed. It is conceivable that the polymerisation observed here is solely due to the close linkage of the Si-H group to the pyridine ring system. With additional units between this group and the ring, it may be possible to negate any effects the ring may impose upon this group. It is also conceivable that it is the catalyst which promotes this undesired reaction and that the use of alternative complexes may promote the hydrosilylation.

On heating 4-vinylpyridine with POSS **2** and chloroplatinic acid in a solution of toluene, a gel-like polymer was rapidly formed. This was dried to yield a slightly rubbery material which proved to be insoluble in a variety of common solvents. As the product of the reaction was expected to be a discrete molecule with a reasonable degree of solubility in solvents such as toluene and dichloromethane, it was assumed that heating the reaction mixture or exposing it to light had caused the 4-vinylpyridine to undergo polymerisation. The experiment was therefore repeated at room temperature with light excluded from the reaction vessel but this produced an identical gel. As it has been demonstrated that vinyl pyridine can be hydrosilylated to hydrido silanes using chloroplatinic acid, it is likely that the catalysts used in these experiments were not responsible for the polymerisation that was observed here. It may be the case that the catalysts used here are not potent enough to promote a rapid reaction between the vinylpyridine and the POSS and polymerisation is occuring before hydrosilylation can occur to any great extent.

In contrast to the experiments using 4-vinylpyridine and derivative **34**, the experiments with 3-vinyldimethylsilylpyridine (**35**) and 4-dimethylvinylsilylmethylpyridine (**38**) only produced polymers when the reaction mixture was heated to 80 °C. At room temperature, these derivatives reacted with POSS **39** to produce what appear to be two new POSS molecules. Due to the nature of the products and the limited time available (these were prepared in the final weeks of the practical phase of this project), it was not possible to purify the samples to a level that would allow accurate analysis. It was possible to study the products using NMR and FTIR spectroscopy and this analysis suggested that the hydrosilylation was successful.

Conclusions

Although these reactions were only a preliminary study, it does appear to be possible to prepare pyridine-functionalised POSS through hydrosilylation of pyridine derivatives to vinyl and silyl POSS. Efforts should now be made to purify these materials to allow analysis to confirm that they are indeed the expected products. If this can be achieved then it may be possible to attempt to prepare extended networks from these molecules through metal co-ordination. Due to the length of the functional groups that appear to have been created, it may not, be possible to prepare well ordered porous materials from them due to the flexibility of these groups. As it appears that hydrosilylation can be used to prepare POSS bearing pyridyl groups, efforts should be made to prepare similar molecules but with fewer atoms between the pyridine ring and the POSS core.

The results from these experiments suggest that the catalysts employed may, in some cases, be incompatible with the species being reacted while in others, may not be potent enough to promote reaction before polymerisation of the pyridine derivative occurs. It may therefore be prudent to investigate the use hydrosilylation catalysts other than chloroplatinic acid and platinum (dvs).

Experimental

General. All reagents and starting materials were prepared as in **Section 3.2**. In addition, platinum (dvs) (Aldrich) was used as supplied. Information on the analytical equipment and techniques is provided in **Appendix B**.

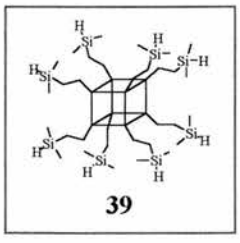
Preparation of 0.01 M chloroplatinic acid solution. Chloroplatinic acid (0.041g, 0.1 mmol) was placed in a 10 cm^3 volumetric flask under a constant flow of argon. The solution was made up with dry isopropanol, capped with an argon blanket and refrigerated for storage.

Preparation of 0.002 M platinum (dvs) solution. Platinum divinyltetramethyldisiloxane in siloxanes (0.096 cm^3, 1.04 M) was placed in a 50 cm^3 volumetric flask under a constant flow of argon. The solution was made up with dry toluene, capped with an argon blanket and refrigerated for storage.

$[SiO_{3/2}H]_8$ (2). Prepared as in **Chapter 2** (page 74).

$[SiO_{3/2}C_2H_3]_8$ (7). Prepared as in **Chapter 2** (page 94).

$[SiO_{3/2}C_2H_4Si(CH_3)_2H$ (39). Dry THF (100 cm^3) was added to **7** (2.030 g, 3.21 mmol) under an argon atmosphere. Dimethylchlorosilane, (9.560g, 101.04 mmol) was added to the solution followed by chloroplatinic acid in isopropanol (8 drops, 0.1 M) and the solution was stirred overnight, as per the method described by Coupar *et al.*[28] The solvent and excess silane were removed and the off-white material obtained was re-dissolved in dry THF (50 cm^3). This solution was added to a suspension of lithium aluminium hydride in THF (100 cm^3) and stirred for 4 hours. The excess lithium aluminium hydride was neutralised with iced dilute hydrochloric acid (250 cm^3, 1M) and the product extracted with diethyl ether (3 × 50 cm^3). After drying over magnesium sulphate, the product was recovered and recrystallised from acetone/ethanol (8 cm^3/12 cm^3) as white needles (1.04 g, 29 %) which analysis confirmed as pure $[SiO_{3/2}C_2H_4Si(CH_3)_2H$ (**39**).[28] ^1H NMR ($CDCl_3$) δ 3.89 (sept, J_{HH}=3.7 Hz, Si**H**, 8H), 0.64 (s, C**H**$_2$, 32H), 0.11 (d, J_{HH}=3.7 Hz, SiC**H**$_3$, 48H). ^{13}C NMR ($CDCl_3$) 5.69 (**C**H_2), 5.07 (**C**H_2), -4.80 (Si**C**H_3). ν_{max}/cm^{-1} (KBr) 2958 (m, CH_2/CH_3), 2921 (w, CH_2/CH_3), 2889 (w, CH_2/CH_3), 2109 (s, SiH), 1406 (m, SiC), 1250 (m, $SiCH_3$), 1106 (s, SiO), 884 (s, $SiCH_3$), 833 (m), 804 (w), 755 (w), 715 (s), 625 (w), 540 (m), 468 (s, SiO). Decomposition begins at 210 °C.


39

Attempted hydrosilylation of POSS 2 with 4-vinylpyridine using chloroplatinic acid at room temperature (40). 4-Vinylpyridine (0.225 g, 2.14 mmol) was added to a solution of **2** (0.110 g, 0.26 mmol) in toluene (15 cm^3) under an argon atmosphere in the dark. Chloroplatinic acid (0.21 cm^3, 0.01 M in isopropanol) was added to the

solution which was then stirred for 24 hours. The solvents and un-reacted vinylpyridine were removed under reduced pressure to leave a red polymeric solid (0.316 g). ν_{max}/cm^{-1} (KBr disk) 2978 (w), 2936 (w), 2260 (w, SiH), 1639 (w), 1607 (m, C=C), 1551 (w), 1467 (w), 1418 (w), 1381 (w), 1156 (s, Si-O), 1065 (vs), 965 (m, $C=CH_2$), 882 (s, Si-H), 839 (m), 794 (w), 764 (w), 564 (w).

Repeating this experiment at 80 °C produced the same polymeric solid. Subsequent experiments using platinum (dvs) at 0.1 mol% gave no reaction at room temperature but formation of the red polymer at 80 °C.

Attempted hydrosilylation of POSS 39 with vinylpyridine using chloroplatinic acid at room temperature (41). 4-Vinylpyridine (0.125 g, 1.19 mmol) was added to a solution of **39** (0.100 g, 0.09 mmol) in toluene (5 cm^3) under an argon atmosphere in the dark. Chloroplatinic acid (0.07 cm^3, 0.01 M in isopropanol) was added to the solution which was then stirred for 24 hours. The solvents and excess vinylpyridine were removed under reduced pressure to leave a red polymeric solid (0.198 g). ν_{max}/cm^{-1} (KBr) 2960 (w, CH_2/CH_3), 2952 (w, CH_2/CH_3), 2895 (w CH_2/CH_3), 2110 (s, SiH), 1639 (w), 1607 (m), 1550 (w), 1467 (w), 1418 (w), 1402 (m), 1381 (w), 1254 (m, $SiCH_3$), 1110 (vs, Si-O), 1065 (vs), 960 (m), 875 (s, $Si-CH_3$), 839 (m), 794 (w), 766 (w), 750 (w), 715 (s), 625 (w), 540 (m), 468 (s, Si-O).

Repeating this experiment at 80 °C produced the same polymeric solid. Subsequent experiments using platinum (dvs) at 0.1 mol% gave no reaction at room temperature but formation of the red polymer at 80 °C.

Attempted hydrosilylation of POSS 7 with derivative 34 using chloroplatinic acid (42). Silyl pyridine **34** (0.130 g, 0.94 mmol) was added to a solution of vinyl POSS **7** (0.050 g, 0.08 mmol) in THF (5 cm^3) under an argon atmosphere in the dark. Chloroplatinic acid (0.06 cm^3, 0.01 M in isopropanol) was added to the solution which was then stirred for 24 hours. The solvents and excess **34** were removed under reduced pressure to leave unreacted **7** (0.049 g). Repeating this experiment at 80 °C produced a colourless polymeric solid (0.169 g). ν_{max}/cm^{-1} (KBr) 3067 (m), 3021 (w), 2986 (w), 2962 (w, CH_2/CH_3), 2952 (w, CH_2/CH_3), 2895 (w CH_2/CH_3), 2107 (s, SiH), 1945 (w), 1639 (w), 1605 (m, C=C), 1550 (w), 1469 (w), 1418 (w), 1409 (s), 1381 (w), 1277 (s), 1257 (m, $SiCH_3$), 1111 (vs, Si-O), 1065 (vs), 1004 (s, $CH=CH_2$), 968 (s, $CH=CH_2$), 884 (s, $SiCH_3$), 839 (m), 794 (w), 778 (s), 766 (w), 750 (w), 715 (s), 704 (w), 625 (w), 573 (s), 564 (w), 540 (m), 463 (m, Si-O).

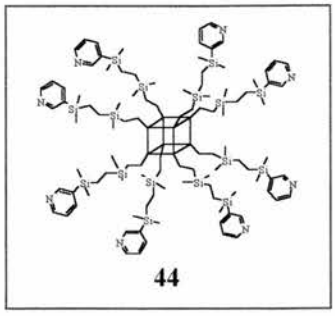
Subsequent experiments using platinum (dvs) at 0.1 mol% also gave the polymeric solid both at room temperature and at 80 °C.

Attempted hydrosilylation of POSS 2 with derivative 35 using chloroplatinic acid at room temperature (43). Vinylsilyl pyridine **35** (1.091 g, mmol) was added to a solution of hydrido cube **2** (0.102 g, 0.24 mmol) in toluene (cm^3) under an argon atmosphere in the dark. Chloroplatinic acid (0.cm^3, 0.01 M in isopropanol) was added to the solution which was then stirred for 24 hours. The solvents and unreacted **35** were removed under reduced pressure to leave unreacted **2** (0.105 g). Repeating the experiment at 80 °C over 4 hours failed to produce any observable product as did repeating the reaction at room temperature with 0.1 mol% platinum (dvs) in place of the chloroplatinic acid. A further experiment using vinylsilyl pyridine **35** (0.210 g,

1.29 mmol), hydrido cube **2** (0.050 g, 0.12 mmol) in toluene (5 cm^3) and platinum (dvs) (0.45 cm^3, 0.002 M in toluene) where the reaction mixture was heated at 80 °C for 10 hours produced a rubbery polymer (0.22 g).

Attempted hydrosilylation of POSS 2 with derivative 38. Vinyldimethylsilylmethyl pyridine **38** (0.394 g, 2.224 mmol) was added to a solution of hydrido cube **2** (0.101 g, 0.238 mmol) in toluene (10 cm^3) under an argon atmosphere in the dark. Chloroplatinic acid (0.19 cm^3, 0.01M in isopropanol) was added to the solution which was then stirred for 24 hours. The solvents and excess **38** were removed under reduced pressure to leave unreacted **2** (0.10 g). This experiment was repeated at 80 °C but again, only unreacted **2** was recovered. Further experiments using 0.1 mol% platinum (dvs) both at room temperature and at 80 °C also failed to produce any observable reaction.

Attempted hydrosilylation of POSS 39 with derivative 35 using chloroplatinic acid. Vinylsilyl pyridine **35** (0.141 g, 0.86 mmol) was added to a solution of **39** (0.051 g, 0.046 mmol) in toluene (5 cm^3) under an argon atmosphere in the dark. Chloroplatinic acid (cm^3, 0.01M in isopropanol) was added to the solution which was then stirred for 24 hours. The solvents and excess **35** were removed under reduced pressure to leave unreacted **39** (0.05 g). This reaction was attempted again at 80 °C for 6 hours but as before, no reaction occurred.



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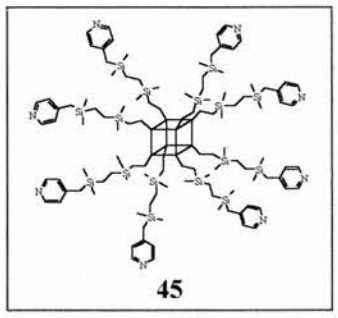
Hydrosilylation of POSS 39 with derivative 35 using platinum (dvs) at room temperature to give product 44. Vinylsilyl pyridine **35** (0.153 g, 0.93 mmol) was added to a solution of **39** (0.050 g, 0.045 mmol) in THF (5 cm^3) under an argon atmosphere in the dark. Platinum (dvs) (0.18 cm^3, 0.002 M in toluene) was added to the solution which was then stirred for 48 hours. The solvents and excess **35** were removed under reduced pressure to leave a pale brown liquid (0.12 g). ^{1}H NMR ($CDCl_3$) δ 8.63 (m, C**H**, 8H), 8.55 (m, C**H**, 8H), 7.80 (m, C**H**, 8H), 7.27 (m, C**H**, 8H), 1.34-0.70 (m, trace), 0.66 (m, C**H**$_2$, 16H), 0.49 (m, C**H**$_2$, 16H), 0.39 (m, C**H**$_2$, 16H), 0.28 (broad s, Si-C**H**$_3$, 48H), 0.09 (m, C**H**$_2$, 16H), -0.06 (broad s, Si-C**H**$_3$, 48H). ^{13}C NMR ($CDCl_3$) δ 153.98 (CN**C**), 149.56 (**C**NC), 140.98 (**C**H), 133.17 (**C**H), 123.11 (**C**H), 6.61 (**C**H$_2$), 6.09 (**C**H$_2$), 4.54 (**C**H$_2$), -2.51 (**C**H$_2$), -4.20 (Si-**C**H$_3$), -4.31 (Si-**C**H$_3$). ν_{max}/cm^{-1} (NaCl, $CDCl_3$) 3050 (w), 2951 (s, CH_2), 2905 (s, CH_2), 2792 (m), 2544 (vw), 2479 (vw), 2302 (vw), 1927 (w), 1584 (m, aromatic ring), 1556 (m, aromatic ring), 1475 (m, aromatic ring), 1407 (s, Si-C), 1333 (w), 1250 (vs, Si-CH_3), 1213 (w), 1110 (vs, Si-O), 1047 (s), 989 (m), 887 (w), 826 (vs, Si-CH_3), 768 (s, CH), 701 (s), 630 (m), 609 (m), 528 (m).

Attempted hydrosilylation of POSS 39 with derivative 38 using chloroplatinic acid. Vinyldimethylsilylmethyl pyridine **38** (0.078 g, 0.440 mmol) was added to a solution of **39** (0.050 g, 0.045 mmol) in THF (5 cm^3) under an argon atmosphere in the dark. Chloroplatinic acid (0.05 cm^3, 0.01 M in isopropanol) was added to the solution which was then stirred for 24 hours. The solvents and excess **38** were removed under reduced pressure to leave unreacted **39** (0.05 g). Repeating the experiment at 80 °C also yield only unreacted **39**.

Hydrosilylation of POSS 39 with derivative 38 using platinum (dvs) at room temperature to give product 45.



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Vinyldimethylsilylmethyl pyridine **38** (0.143 g, 0.806 mmol) was added to a solution of hydrido cube **39** (0.100 g, 0.090 mmol) in THF (5 cm^3) under an argon atmosphere in the dark. Platinum (dvs) (0.36 cm^3, 0.002 M in toluene) was added to the solution which was then stirred for 48 hours. The solvents and excess **38** were removed under reduced pressure to leave a pale brown liquid (0.12 g). ^1H NMR ($CDCl_3$) δ 8.34 (broad s, C**H**, 16H), 6.90 (broad s, C**H**, 16H), 2.09 (s, C$\underline{\mathbf{H}}_2$, 16H), 0.56 (m, C$\underline{\mathbf{H}}_2$, 16H), 0.53 (m, C$\underline{\mathbf{H}}_2$, 16H), 0.38 (m, C$\underline{\mathbf{H}}_2$, 16H), 0.34 (m, C$\underline{\mathbf{H}}_2$, 16H) 0.08 (m), 0.0 (m), -0.11 (s, Si-C$\underline{\mathbf{H}}_3$, 72H). ^{13}C NMR ($CDCl_3$) δ 149.29 and 149.00 (CH and –CH_2-$\underline{\mathbf{C}}$-$(CH)_2$), 123.58 ($\underline{\mathbf{C}}$H), 25.35 ($\underline{\mathbf{C}}H_2$), 6.63 ($\underline{\mathbf{C}}H_2$), 6.14 ($\underline{\mathbf{C}}H_2$), 4.50 ($\underline{\mathbf{C}}H_2$), -2.57 ($\underline{\mathbf{C}}H_2$), -4.20 (Si-$\underline{\mathbf{C}}H_3$), -4.43 (Si-$\underline{\mathbf{C}}H_3$). ν_{max}/cm^{-1} (NaCl, $CDCl_3$) 3052 (m), 2953 (s, CH_2), 2901 (s, CH_2), 2793 (m), 2663 (w), 2544 (vw), 2481 (vw), 2304 (vw), 2216 (vw), 2107 (vw), 2031 (vw), 1931 (w), 1846 (vw), 1731 (vw), 1680 (vw), 1600 (m, aromatic ring), 1556 (m, aromatic ring), 1493 (m, aromatic ring), 1416 (s, Si-C), 1337 (w), 1251 (vs, Si-CH_3), 1214 (m), 1116 (vs, Si-O), 1054 (vs), 993 (m), 899 (m), 837 (vs, Si-CH_3), 761 (s), 738 (s), 706 (s), 633 (m), 603 (m), 559 (m), 537 (m).

3.5 General Conclusions

The direct combination of lithiated pyridines with chlorosilane-functionalised POSS does not appear to be a viable route to the preparation of highly functionalised POSS. While a number of the chlorosilane groups are modified in the expected

manner, the yield of this reaction is not high enough to produce POSS suitable for the preparation of extended networks. One of the problems with this approach is that the mixed functionality POSS produced cannot be purified as the by-products are bound to the same molecule as the desired products.

The solution to this problem appeared to be the use of hydrosilylation to provide a high yielding reaction. To this end, attempts were made to prepare pyridine derivatives suitable for hydrosilylation and two new molecules were prepared. Attempts were then made to hydrosilylate these derivatives, 4-vinyl pyridine and dimethylsilylpyridine to hydrido and vinyl-functionalised POSS. These experiments made use of both chloroplatinic acid and platinum (dvs) catalysts, but no reaction using chloroplatinic acid was successful. The majority of the experiments using platinum (dvs) either failed or polymerisation of the derivative appeared to take place. Two experiments show promising results however, and produced materials that appear to be two new types of POSS. Time did not allow for full analysis of these materials, but NMR and FTIR data suggest that they are indeed discrete pyridine-functionalised POSS.

The outcome of these experiments suggest that if platinum-based hydrosilylation catalysts are to be employed, the reacting groups must not be connected directly to either the POSS core or the pyridine ring, but further studies are required to confirm this. It may be the case that non-platinum catalysts will promote reaction between the other derivative-POSS pairs investigated here. There is already evidence that the use of a rhodium catalyst can be employed successfully with

vinylpyridine while the experiments performed here using platinum catalysts either produced polymers or no reaction at all when vinylpyridine was the vinyl source.

If it can be confirmed that the two products which are suspected to be pyridine-functionalised POSS are indeed what they appear to be, it may be possible to attempt linking these POSS through metal co-ordination. Although it is assumed that pyridine moieties such as those suspected to be bound to the POSS will co-ordinate readily with, for example, silver (I), the lengthy functional groups may be too flexible to permit the assembly of well ordered structures.

3.6 Bibliography

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Chapter 4 Miscellaneous Reactions

4.1 General Introduction

In the early stages of this project a variety of reactions were attempted in an effort to identify synthetic techniques which could be utilised to produce useful functionalised POSS. Techniques allowing the preparation of a variety of products in high yields were of particular interest and three synthetic strategies of this type were investigated. These experiments were undertaken with no specific target molecules in mind and are therefore described in this chapter rather than the earlier goal-orientated sections.

Heck-type arylations are reactions catalysed by palladium complexes which form carbon-carbon bonds between aryl halides and vinyl groups with retention of the double bond.[1] Although yields depend on the composition of the reaction mixture, a variety of aryl halides can be used[2] making this a potentially useful reaction and a study was made into its use with vinyl-functionalised POSS.

Feher and Budzichowski prepared a POSS bearing chloromethylphenyl groups[3] which appears to be an ideal precursor for molecular building blocks but the molecule is very unreactive making it very difficult to convert the chloro groups into groups suitable for self assembly. The Gabriel synthesis[4] is a series of reactions through which even unreactive halide groups[5] can be converted to amines *via* a phthalimide-bearing molecule and appeared to offer a means by which Feher and Budzichowski's POSS could be modified. Although this project was not directed

towards the preparation of amines, with amine groups in place of the chloro groups further manipulation of this POSS may be possible and attempts were therefore made to use this synthetic pathway.

Radical reactions with vinyl groups can be high yielding and a series of experiments were performed to investigate the possibility of using this type of reaction with vinyl functionalised POSS $[SiO_{3/2}C_2H_3]_8$ (**7**). Due to the variety of commercially available thiols and their general stability when converted into free radicals, this class of molecule was used to provide the radical species for these experiments.

Even if these experiments did not produce molecules suitable for use in self-assembling networks, information gleaned from their outcome was expected to assist in other areas of this project.

4.2 Heck Type Arylation of Octavinyl POSS

Introduction

The Heck-type arylation reaction is a palladium catalysed process which can be used to produce arylated alkenes from aryl halides and alkenes.[1] A palladium (II) complex forms the core of the catalyst system with the complex ligands and the composition of the reaction mixture governing how effective it is.[6, 7, 8] There is still debate over the details of the reaction mechanism but it has been proposed that the

palladium species binds to the aryl halide and then acts to co-ordinate the resultant intermediate to the vinyl group before establishment of the carbon-carbon bond and release of the palladium.[9]

Vinyltrimethylsilane and vinyltriethoxysilane have both been successfully combined with a wide variety of aryl halides[2, 10, 11] making this type of reaction of particular interest for this project. The success of the reactions using discrete vinylsilanes, albeit in yields below 100%, suggested that the reaction would be viable with vinyl functionalised POSS such as $[SiO_{3/2}C_2H_3]_8$ (**7**). As well as allowing a variety of aryl halides to be used, this methodology also produces arylated species with retention of the double bond, which should provide a degree of rigidity to any functionalised POSS molecules synthesised in this way.

When vinyl silanes are used in this type of reaction they can undergo de-silylation but Karabelas *et al* found that this effect can be greatly reduced by the introduction of silver nitrate into the reaction mixture.[2] The presence of silver ions has the additional benifit of increasing the rate of reaction, possibly by abstracting the halide atom from the palladium/alkyl halide complex (***Figure 4.1***).

Several palladium complexes can be used as catalysts for Heck-type arylations but some are more efficient than others. Two commonly used examples are palladium (II) chloride and palladium (II) acetate with the latter having been described as the more effective catalyst for this type of reaction.[2] Contrary to previous reports it was found that palladium (II) chloride could produce satisfactory results under the reaction conditions employed in this study and was therefore used in all of these experiments.

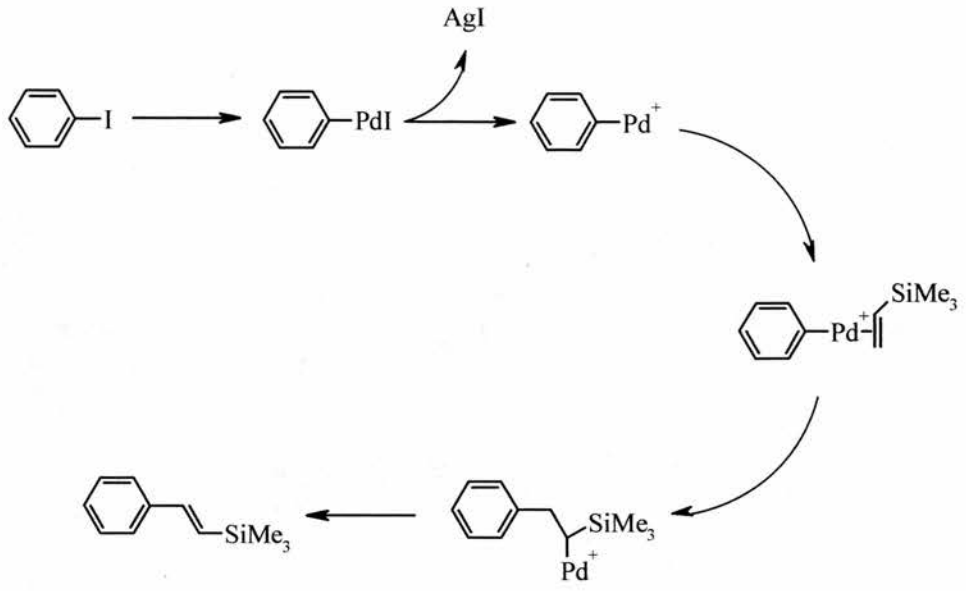

Figure 4.1. *Reaction mechanism for the silver-stabilised Heck type arylation of vinyl silanes proposed by Karbelas and Halberg.*[2]

Since the original reaction using a palladium (II) acetate complex was described by Heck, improvements have been made to the composition of both the complex and the reaction mediums used to render the catalyst system more efficient.[6, 7, 8]

Although the goal of these experiments was to prepare POSS with functional groups capable of being linked together, 4-iodotoluene was selected as the aryl halide for the preliminary experiments to reduce the possibility of side reactions. If successful reaction was observed using this aryl halide, it was intended that further studies would be undertaken using a variety of aryl halides to prepare a range of POSS.

Results and Discussion

Although a reaction has taken place between the POSS and 4-iodotoluene it proceeded in low yield to give a mixture of mono- and di-arylated POSS (***Figure 4.2***).

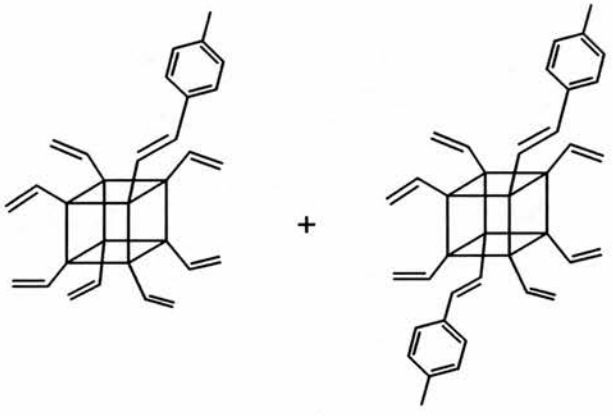

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Figure 4.2. *Two POSS that may be contained in the product of the palladium (II) chloride-catalysed reaction between octa-vinyl POSS* ***7*** *and 4-iodotoluene (****46****).*

It was suspected that the low yield may be due to the catalyst used and the reaction conditions, but upon repeating the experiment using trimethylvinylsilane in place of the POSS, (E)-trimethyl-[2-(methylphenyl)ethenyl)]-silane (**48**, ***Figure 4.3***) in a yield of 77% was obtained. This yield was higher than that obtained by Karabelas and Hallberg using palladium acetate,[2] indicating that the reaction conditions employed were indeed satisfactory.

The yield of the reaction does not appear to be concentration related as varying the quantity of iodotoluene does not affect the number of vinyl groups that are arylated. By decreasing the quantity of aryl halide and catalyst available for reaction, it was thought that a lower yield would be obtained but this was not observed and the

product (**47**) appears to be identical to **46**. It has been shown previously that Heck-type arylations with trimethylvinylsilane as the olefin source give considerably higher yields than those using triethoxyvinylsilane suggesting that the low yield is due to the electron-withdrawing effect of the cube.

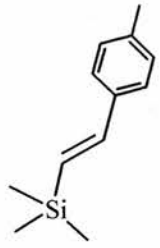

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Figure 4.3. *(E)-trimethyl-[2-(methylphenyl)ethenyl)]-silane (**48**)*

There is also the possibility that steric hindrance may affect the outcome of the reaction. As the yield of reacted groups does not appear to exceed an average of 2 per cube, it may be the case that diametrically opposite vinyl groups are reacting to produce the least sterically demanding product. The conformation of the product would be very difficult to verify but it is irrelevant with regard to this project, as the reaction yield is not high enough to allow synthesis of molecules suitable for self-assembling porous networks.

Conclusions

Heck-type arylation appears to be viable with vinyl functionalised POSS but only in low yield. The yields obtained using the reaction conditions studied here are relatively high when trimethylvinylsilane is used but are dramatically lower when a

vinyl POSS is used. This indicates that the electron withdrawing effect of the POSS core and/or steric constraints contribute to this low yield.

In previous studies it has been assumed that the rate determining step in this type of arylation is the binding of the palladium species to the aryl halide.[2, 9] The difference in yield between reactions using vinyl POSS and those using vinyl silanes observed here suggests that the outcome of the reaction is also dependent on the nature of the vinyl bearing species. The efficiency of many of the current catalyst systems is due to superior interaction between the catalyst and the aryl halide which could mean that they may only promote a slight improvement in the yield of vinyl POSS reactions.

Many options are available for further work in this area, but the large number of variations in reaction mixture and conditions that are possible led to the decision being made to postpone further work until potentially more profitable routes were investigated.

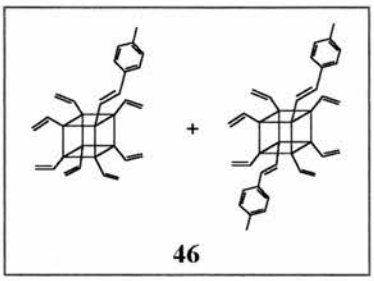
Experimental

General. Palladium chloride (Johnson Matthey Chemicals Ltd), triphenylphosphine (Lancaster), silver nitrate (Lancaster), 4-iodotoluene (Cambrian Chemicals), diethyl ether (BDH), magnesium sulphate (Fisher), trimethylvinylsialne (Aldrich) were used as supplied. Acetonitrile (Ultrafine Ltd) was dried over Linde 4A molecular sieves (Prolabo) and distilled from calcium hydride (Aldrich) immediately before use. Triethylamine (Lancaster) was refluxed over potassium hydroxide (Fisher) and

distilled from calcium hydride (Aldrich) immediately before use. Information on the analytical equipment and techniques is provided in **Appendix B**.

Preparation of $[SiO_{3/2}C_2H_3]_8$ (7). Prepared as in **Chapter 2** (page 94).

Heck-type arylation using excess iodotolene (46). Dry acetonitrile (50 cm^3) was added to a mixture of palladium chloride (0.0244 g, 0.14 mmol), triphenylphosphine (0.0666 g, 0.25 mmol), silver nitrate (1.02 g, 6.00 mmol), triethylamine (0.3000 g, 2.96 mmol), 4-iodotoluene (1.32 g, 6.05 mmol) and **7** (0.3000 g, 0.47 mmol) under an argon atmosphere. The resultant mixture was then stirred at reflux for 5 days. After cooling, the solids were removed by filtration. The filtrate was added to water (100 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined organic components were dried over magnesium sulphate and the solvent was removed under reduced pressure to give a dark brown oil. Column chromatography of this oil (220 - 440 mesh silica gel, diethyl ether elutant) yielded an orange solid which was subjected to vacuum sublimation (130 °C, 24 mmHg). Unreacted iodotoluene (0.89 g) was removed by this process leaving a dark brown residue which was subjected to column chromatography to give a pale orange oil (0.37 g). ^{1}H NMR ($CDCl_3$) δ 7.72 (m, -C**H**=CH-, 2H), 7.53 (m, C**H**=CH, 2H), 7.48 (d, J_{HH}=8.4 Hz, C**H**, 4H), 7.17 (d, J_{HH}=8.3 Hz, C**H**, 4H), 6.26-5.68 (m [individual peaks broadened], C**H**=C**H**$_2$, 18H), 2.39 (s, C-C**H**$_3$, 6H). ^{13}C NMR ($CDCl_3$) δ 139.20 (C=**C**H-C), 137.76 (**C**-CH_3), 137.02 (CH_2=**C**H), 134.89 (**C**-CH=C), 129.34 (C=**C**H-Si), 128.69 (**C**H_2=CH), 128.12 (**C**H), 126.31 (**C**H), 19.78 (**C**H_3). ν_{max}/cm^{-1} ($NaCl/CDCl_3$) 2919 (vw, CH_3), 2847 (vw), 1702 (w), 1603 (m, C=C), 1457



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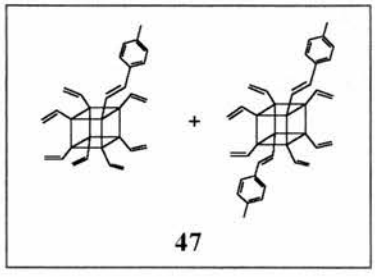
(w, CH_3), 1407 (m, Si-C), 1361 (w, CH_3), 1278 (m), 1120 (s, Si-O), 1004 (s, $CH=CH_2$), 980 (w, CH=CH), 966 (m, $CH=CH_2$), 812 (w, aryl CH), 769 (m), 721 (m), 585 (s), 529 (w), 469 (s, Si-O). CHN microanalysis: Calculated for $(SiO_{3/2})_8(C_2H_3)_7(C_9H_9)$ 38.20 % C, 4.18 % H. Calculated for $(SiO_{3/2})_8(C_2H_3)_6(C_9H_9)_2$ 44.30 % C, 4.46 % H. Found 43.91 % C, 5.40 % H.

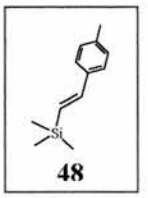
Heck-type arylation using insufficient iodotolene (47). Dry acetonitrile (50 cm^3) was added to a mixture of palladium chloride (0.0110 g, 0.06 mmol), triphenylphosphine (0.0330 g, 0.13 mmol), silver nitrate (0.034 g, 0.13 mmol), triethylamine (0.270 g, 2.67 mmol), 4-iodotoluene (0.431 g, 1.97 mmol) and **7** (0.311 g, 0.49 mmol) under an argon atmosphere. The resultant mixture was then stirred at reflux for 5 days. After cooling, the solids were removed by filtration. The filtrate was added to water (100 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined organic components were dried over magnesium sulphate and the solvent was removed under reduced pressure to give a dark brown oil. Column chromatography of this oil (220 - 440 mesh silica gel, diethyl ether elutant) yielded an orange solid which was subjected to vacuum sublimation (130 °C, 24 mmHg) to give a pale orange oil (0.29 g). ^{1}H NMR ($CDCl_3$) δ 7.72 (m, -C**H**=CH-, 2H), 7.53 (m, -C**H**=CH-, 2H), 7.48 (d, J_{HH}=8.3 Hz, C**H**, 4H), 7.17 (d, J_{HH}=8.3 Hz, C**H**, 4H), 6.26-5.68 (m [individual peaks broadened], C**H**=C**H**$_2$, 18H), 2.39 (s, C-C**H**$_3$, 6H). ^{13}C NMR ($CDCl_3$) δ 139.20 (C=**C**H-C), 137.76 (**C**-CH_3), 137.01 (CH_2=**C**H), 134.89 (**C**-CH=C), 129.34 (C=**C**H-Si), 128.69 (**C**H_2=CH), 128.12 (**C**H), 126.31 (**C**H), 19.78 (**C**H_3). ν_{max}/cm^{-1} (NaCl/$CDCl_3$) 2920 (vw, CH_3), 2845 (vw), 1702 (w), 1604 (m, C=C), 1453 (w, CH_3), 1407 (m, Si-C), 1363 (w, CH_3), 1278 (m), 1120



47

(s, Si-O), 1003 (s, CH=CH_2), 980 (w, CH=CH), 961 (m, CH=CH_2), 813 (w, aryl CH), 774 (m), 721 (m), 584 (s), 529 (w), 465 (s, Si-O).

(E)-Trimethyl-[2-(4-methylphenyl)ethenyl)]-silane (48). Dry acetonitrile (75 cm^3) was added to a mixture of palladium chloride (0.0294 g, 0.17 mmol), triphenylphosphine (0.0785 g, 0.30 mmol), silver nitrate (0.85 g, 5.00 mmol), triethylamine (0.73 g, 7.21 mmol), 4-iodotoluene (1.11 g, 5.09 mmol) and vinyltrimethylsilane (0.98 g, 9.78 mmol) under an argon atmosphere. The mixture was stirred at reflux for 6 hours, cooled and then filtered. The filtrate was added to water (100 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined organic components were dried over magnesium sulphate and the solvent was removed under reduced pressure. Column chromatography (220-440 mesh silica gel, diethyl ether elutant) of the material obtained produced a pale yellow oil (0.75 g, 77 % yield). ^{1}H NMR ($CDCl_3$) δ 7.41 (d, C**H**, 2H, J_{HH}=8.1) 7.03 (d, C**H**, 2H, J_{HH}=8.1), 6.80 (d, C=C**H**-C, J_{HH}=19.5 Hz, 1H), 6.46 (d, C=C**H**-Si, J_{HH}=19.5 Hz, 1H), 2.32 (s, C-C**H**$_3$, 3H), 0.15 (s, Si-C**H**$_3$, 9H). ^{13}C NMR ($CDCl_3$) δ 143.47 (C=**C**H-C), 137.76 (**C**-CH_3), 135.69 (**C**-CH=C), 129.18 (C=**C**H-Si), 128.12 (CH), 126.26 (CH), 21.20 (C-**C**H_3), -1.20 (Si-**C**H_3). ν_{max}/cm^{-1} (NaCl/$CDCl_3$) 2952 (m, CH_3), 1607 (m, aryl C), 1565 (w, aryl C), 1510 (m, aryl C), 1435 (w, CH_3), 1406 (m, Si-C), 1247 (s, Si-CH_3), 1176 (m), 1110 (w), 1036 (w), 996 (w), 986 (s, CH=CH), 865 (s, $Si(CH_3)_3$), 830 (s, aryl CH), 727 (m), 690 (w), 617 (w), 496 (m).



48

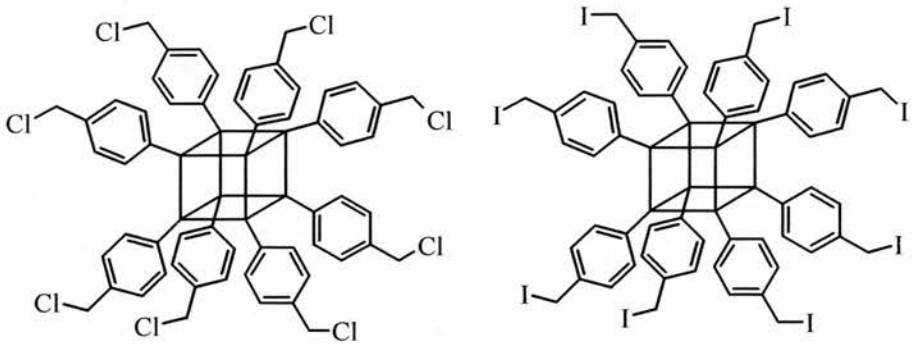
4.3 Gabriel Synthesis with Octaiodomethylphenyl POSS

Introduction

Feher and Budzichowski prepared 1,3,5,7,9,11,13,15-octakis[4-(iodomethyl)phenyl]pentacyclo[9.5.1.$1^{3,9}$.$1^{5,15}$.$1^{7,13}$]octasiloxane (**49**) through the hydrolytic condensation of 4-(chloromethyl)phenyltrichlorosilane (***Figure 4.4***).[3] Although this molecule would appear to be an ideal precursor for the synthesis of a wide variety of functionalised silsesquioxanes, they found that the chloro groups of this POSS are very unreactive. Irrefutable evidence has not been provided but it has been suggested that the lack of reactivity is due to the electron withdrawing effect of the silicon/oxygen core acting through the ring systems to deactivate these groups.[3] Despite the unreactive nature of the chloro functionalised POSS, it is possible to convert the chloromethyl groups to iodomethyl in a halogen exchange reaction. The 1,3,5,7,9,11,13,15-octakis[4-(iodomethyl)phenyl]pentacyclo[9.5.1.$1^{3,9}$.$1^{5,15}$.$1^{7,13}$]-octasiloxane (**50**) produced, is slightly more reactive than the chloro form and can be used in a limited number of reactions.

Despite their inert nature, the rigidity of the functional groups make these molecules potentially useful starting materials for the creation of POSS for use in porous networks. The reactions employed by Feher and Budzichowski to modify these molecules do not produce POSS suitable for self-assembly and attempts were therefore made to find more appropriate synthetic strategies. Although many reactions involving halomethyl groups have been reported, the use of a modified version of the

Gabriel synthesis[5] appeared to offer a likely means by which **50** and **51** could be transformed into useful POSS.



49 **50**

Figure 4.4. *$[SiO_{3/2}C_6H_4CH_2Cl]_8$ **(49)** and $[SiO_{3/2}C_6H_4CH_2I]_8$ **(50)** developed by Feher and Budzichowski.*[3]

The Gabriel synthesis is a series of reactions that can be used to produce a primary amine from an alkylhalide.[4, 12] In the reaction originally described by Gabriel, an alkylphthalamide is prepared by reacting the alkylhalide with potassium phthalamide. The phthalamide groups are then cleaved in an acid- or base-catalysed hydrolysis reaction to yield the amine (***Figure 4.5***).

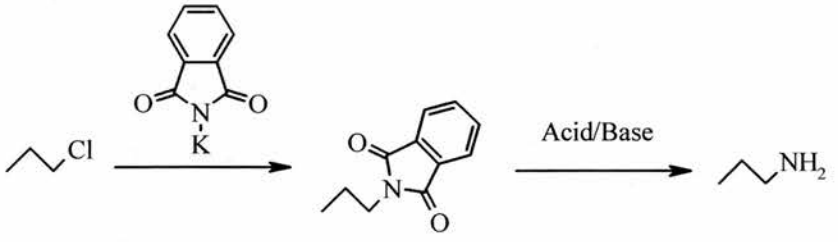


Figure 4.5. *Schematic of the basic Gabriel synthesis.*

Recent improvements to the reaction sequence allow this process to be used with very inert halides[5] and have made the hydrolysis step more efficient.[13] This suggested that the initial step of the reaction scheme would be viable with **49** and that

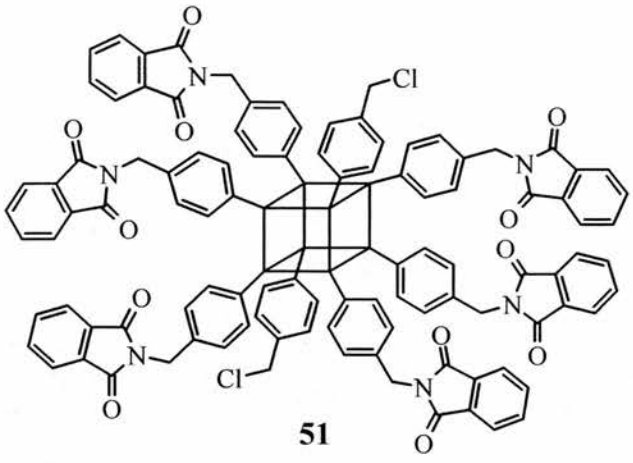
the hydrolysis step could be performed in such a way as to avoid damage to the POSS core or cleavage of the functional groups.

Initially, an attempt was made to perform the reaction with the chloro form of the POSS (**49**) followed by a more successful reaction with the more active iodo form (**50**). Due to the yields obtained, only the first stage of the Gabriel synthesis was undertaken.

Results and Discussion

Preparing **49** using the procedure described by Feher and Budzichowski resulted in recovered yields of less than 3 % compared with the reported yield of 6.1 %. By performing the reaction on one tenth of the original scale and allowing the product to precipitate over 3 days after the reaction mixture had cooled, yields as high as 4.7 % were obtained. Conversion of **49** to **50** proceeded as expected with pure **50** being recovered in over 90 % yield.

Attempts were made to react potassium phthalamide with both **49** and **50** in DMF using the method described by Sheehan and Bolhofer.[5] Although it had been reported that performing the reaction in this manner produced good yields from inert halides, no reaction could be detected between the potassium phthalamide and **49**. Repeating the experiment using **51** resulted in an exothermic reaction with approximately 75 % (based on ^{1}H NMR data) of the iodomethyl groups reacting successfully, while the remainder were converted back to the chloro form during the work up to produce **51** (***Figure 4.6***).



51

Figure 4.6. *A possible structure for product **51**. The experimental data does not reveal which corners of the POSS cube are occupied by moieties containing phthalamide groups and only gives an average for the total number of phthalamide groups per cube.*

The 75% yield suggested by the peak areas of the ^{1}H NMR spectra is apparently confirmed by the carbon content determined by CHN microanalysis but this is not consistent with the nitrogen content which indicates a higher yield. This suggests that there is a by-product or contaminant present which is masked by some of the broad, overlapping peaks of the ^{1}H NMR spectra and present in levels too low to be clearly detected by ^{13}C NMR spectra. Had this element of the project been continued, cleavage of the phthalamide groups could have reduced, if not removed, some of the broader peaks from the ^{1}H NMR allowing clear identification of contaminants and by-products.

While **50** does react with potassium phthalamide, **49** does not which suggests that the reactivity of the POSS functional groups has a considerable effect on the reaction. Steric hindrance may also affect the outcome of the reaction as the

phthalamide groups are relatively large but without modelling of the system using less hindered structures, the effect of steric hindrance cannot be assessed.

A yield of approximately 75 % in a primary reaction step is not high enough to meet the requirements of this project. Raising the reaction temperature above 100 °C had little effect on the yield, nor did varying the amount of potassium phthalamide added suggesting that it may not be possible to increase the yield without a major change to the experimental procedure. With only 75 % of the POSS functional groups bearing phthalamide units, subsequent reactions with low or moderate yields would produce POSS with only a small number of the desired groups. As the reactions which could be used to convert the phthalamide groups into moieties suitable for self assembly are unlikely to generate yields close to 100 %, the hydrolysis of these groups was not investigated.

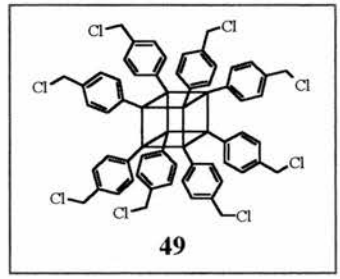
Conclusions

The optimised reaction conditions for the first step of the Gabriel synthesis described by Sheehan *et al*[5] cannot modify chloromethylphenyl POSS **49** but can covert approximately 75 % of the iodomethylphenyl groups bound to POSS **50**. As this is only the first step in a series of reactions, a high yield is required to compensate for any low or even moderate yielding reactions in subsequent steps if highly functionalised POSS are to be prepared and this particular route to functionalised silsesquioxanes was therefore abandoned.

Experimental

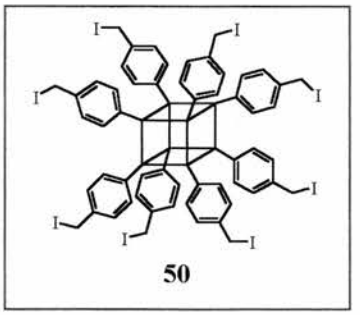
General. 4-(Chloromethyl)phenyl-trichlorosilane (Lancaster), acetone (Fisher), sodium iodide (Fisher), THF (Fisher), dichloromethane (Fisher), DMF (Aldrich), potassium phthalamide (Lancaster), magnesium sulphate (Fisher) and argon (BOC) were used as supplied. Information on the analytical equipment and techniques is provided in **Appendix B**.

Preparation of $[SiO_{3/2}C_6H_4CH_2Cl]_8$ 1, 3, 5, 7, 9, 11, 13, 15-Octakis{2-[4-(chloromethyl)phenyl]ethyl}-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (49). 4-(Chloromethyl)phenyl-trichlorosilane (3.21 g, 12.3 mmol) was added to an 80 % acetone/water solution and was heated at reflux for 3 days in the manner described by Feher *et al.*[3] A white powder (0.10 g, 5 % yield) was recovered from the cooled reaction mixture after 3 days and analysis confirmed it as the chloromethylphenyl-functionalised POSS previously reported.[3] ^{1}H NMR ($CDCl_3$) δ 7.77 (d, J_{HH} = 8.4 Hz, C**H**, 2H) 7.44 (d, J_{HH} = 8.3 Hz, C**H**, 2H), 4.61 (s, C**H**$_2$, 2H). ^{13}C NMR ($CDCl_3$) δ 140.22 (**C**-CH_2), 134.22 (**C**H), 129.87 (**C**-Si), 128.11 (**C**H), 45.92 (C-**C**H_2). υ_{max}/cm^{-1} (KBr disc) 3063 (w, aryl CH), 3019 (w, aryl CH), 2950 (w, CH_2), 1605 (w, aryl C), 1398 (w, C-Si), 1264 (w), 1191 (m), 1127 (s, Si-O), 1022 (m), 832 (m, aryl CH), 814 (w), 736 (w), 700 (m, C-Cl), 674 (w), 587 (m), 520 (m), 479 (m, Si-O). Decomposition begins at 250 °C.



49

Preparation of $[SiO_{3/2}C_6H_4CH_2I]_8$, 1, 3, 5, 7, 9, 11, 13, 15-Octakis{2-[4-(iodomethyl)phenyl]ethyl}-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (50).



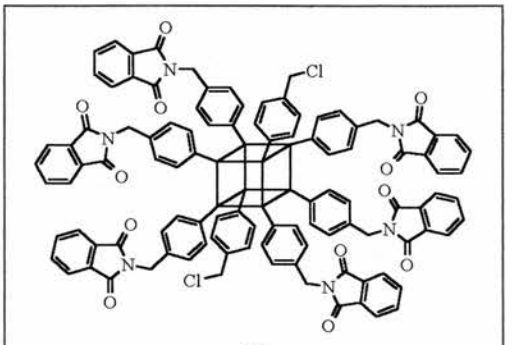
50

Sodium iodide (4.20 g, 28.04 mmol) and **49** (0.200 g, 0.14 mmol) were refluxed overnight in THF (25 cm^3) in the manner described by Feher *et al.*[3] On cooling, the reaction mixture was filtered, the solids were washed with dichloromethane (10 cm^3) and the solvents were removed from the combined organic components to leave a moist solid. This material was extracted with dichloromethane (3 × 10 cm^3) and the pale yellow solid obtained from this solution was recrystallised from acetone/dichloromethane to give small off-white crystals (0.27 g, 90 % yield). Analysis confirmed that this was the iodomethylpheny-functionalised POSS previously reported.[3] ^{1}H NMR ($CDCl_3$) δ 7.66 (d, J_{HH} = 8.1 Hz, C**H**, 2H), 7.41 (d, J_{HH} = 8.0 Hz, C**H**, 2H), 4.46 (s, C$\underline{\mathbf{H}}_2$, 2H). ^{13}C NMR ($CDCl_3$) δ 142.06 (**C**-CH_2), 134.64 (**C**H), 129.30 (**C**-Si), 128.28 (**C**H), 4.97 (C-**C**H_2). υ_{max}/cm^{-1} (KBr disk) 3020 (w, aryl CH), 2950 (w, CH_2), 1600 (w, aryl C), 1400 (w, Si-C), 1240 (w), 1200 (m), 1120 (s, Si-O), 1020 (m), 840 (w, aryl CH), 820 (w), 736 (w), 700 (m), 674 (w), 587 (m), 520 (m, CI), 479 (m, Si-O). Decomposition begins at 240 °C.

Attempted Gabriel synthesis using 49. Dry DMF (15 cm^3) was added to **49** (0.200 g, 0.14 mmol) under an argon atmosphere and a solution of potassium phthalimide (0.402g, 2.17 mmol) dissolved in dry DMF (10 cm^3) was added dropwise with constant stirring. No reaction was observed and the solution was heated to 100 °C for 10 hours with constant stirring. On cooling the reaction mixture was added to water (100 cm^3) and extracted with dichloromethane (3 × 50 cm^3). The combined organic

components were dried over magnesium sulphate and the solvents were removed under reduced pressure to yield unreacted **49** (0.18 g).

Gabriel synthesis using 50 (51). Dry DMF (20 cm^3) was added to **50** (0.500 g, 0.23 mmol) under an argon atmosphere and a solution of potassium phthalimide (0.650 g, 3.51mmol) dissolved in dry DMF (10 cm^3) was added drop-wise with constant stirring.



51

A slight exotherm was observed during the addition with the elevated temperature being maintained for a short period after all the phthalimide solution had been added. The solution was then heated to 100 °C with stirring for 10 hours. After cooling, the reaction mixture was added to water (100 cm^3) and extracted with dichloromethane (3 × 50 cm^3). The combined organic components were dried over magnesium sulphate and the solvents were removed under reduced pressure. Attempts to recrystallise the product from dichloromethane were unsuccessful with the product forming colloidal particles as the solution cooled. The product was recovered as a waxy yellow solid (0.31 g). ^{1}H NMR ($CDCl_3$) δ 7.83 (broad s, C**H**, 12H), 7.73 (broad s, C**H**, 12H), 7.65 (d, J_{HH} = 8.0 Hz, C**H**, 4H), 7.45 (broad m, C**H**, 24H), 7.39 (d, J_{HH} = 8.0 Hz, C**H**, 4H), 4.70 (broad s, C$\mathbf{H}_2$N, 12H), 4.60 (s, C$\mathbf{H}_2$Cl, 4H). ^{13}C NMR ($CDCl_3$) δ 167.69 (**C**=O), 140.00 (**C**-CH_2), 134.53 (**C**H), 133.91 (**C**H), 132.10 (**C**H), 129.05 (**C**-Si), 127.67 (**C**H), 123.38 (**C**-C=O), 45.92 (**C**H_2-Cl), 41.44 (**C**H_2-N). υ_{max}/cm^{-1} (KBr disk) 3041 (w, aryl CH), 3017 (w, aryl CH), 2920 (w, CH_2), 2848 (w, NCH_2), 1771 (m, NC=O), 1712 (s, NC=O), 1656 (m), 1604 (m, aryl C), 1467 (m), 1426 (m), 1390 (s, C-Si), 1346 (m), 1301 (m), 1123 (s, Si-O), 1081 (s), 1017 (m), 936 (m), 792 (m), 714 (m,

aryl CH), 691 (w, CCl), 615 (w), 553 (w), 494 (m, Si-O). CHN microanalysis: Calculated for $(SiO_{3/2})_8(C_6H_4CH_2Cl)_2(C_6H_4CH_2NC_8H_4O_2)_6$ 59.90 % C, 3.48 % H, 4.03 % N. Found 60.52 % C, 3.60 % H, 4.67 % N. Decomposition begins at 220 °C.

4.4 Reactions of Octavinyl POSS with Aromatic Thiols

Introduction

Free radicals can react readily with functional groups containing double bonds with numerous examples being reported.[14, 15, 16] As octavinyl POSS **7**, $[SiO_{3/2}C_2H_3]_8$, is easily prepared its ability to react with radicals was investigated as a possible route to new functionalised POSS. Although there are many possible radical sources available, thiophenols possess several qualities that are desirable for the purposes of this project. Aromatic thiols of this type can be readily converted into stable radical species by homolytic cleavage of the sulphur-hydrogen bond using chemical,[17] UV[18] or electrochemical[19] initiation. As well as being relatively easy to convert into a radical, this class of molecule has a ring system which provides a rigid, sterically demanding group which could prove useful in extended POSS structures. Thiophenol itself was an ideal model molecule with which to attempt the reaction due to its lone functional group and derivatives such as aminothiophenol which offer the possibility of producing POSS with moieties ending in potentially useful groups.

Many reactions have been reported where thiols have been reacted with vinyl silanes with varying degrees of success.[20, 21, 22] A large proportion of these reactions

were performed with a view to preparing sulfinyl derivatives and the material produced through the thiol/vinyl reaction was not isolated, leading to a lack of information on the yields of these intermediate molecules. The final yields from these reaction sequences are high however, suggesting that the reactions between thiols and vinyl groups are also high yielding.

Seshadri and Haupt reported the preparation of chromatography column packing *via* radical reactions of triethoxyvinylsilane with thiophenol as well as 2-, 3- and 4-aminothiophenols, giving yields of 65%, 70%, 65% and 85% respectively.[23] Despite the yields of these reactions being less than 90% it was considered worth investigating this approach if the reaction of thiophenol with the cube proved viable.

Even without an external directing influence, radicals derived from thiophenols react exclusively at the terminal carbon of vinyl silane groups producing an intermediate which abstracts a proton from another thiophenol, regenerating the active thiyl species and resulting in a chain reaction (***Figure 4.7***).[24] It has been suggested that the terminal carbon is favoured as it is the least sterically hindered and results in the formation of a resonance-stabilised intermediate.[25] For the purposes of this project, the favouring of one carbon over the other is ideal as uniformly functionalised cubes would be generated.

Initially, a series of experiments were undertaken in an effort to find an effective method of reacting thiophenol with the vinyl cube. Once it had been demonstrated that this type of reaction was possible, an attempt was made to react 4-aminothiophenol with **7** to produce a more useful molecule. Of the several types of

initiation that are applicable to thiophenols, chemical initiation using azo-isobutyronitrile (AIBN) was chosen for practicality and simplicity. Heating in air was an alternative[22] but this was known to promote the formation of disulphides and was therefore avoided to make the work up easier.

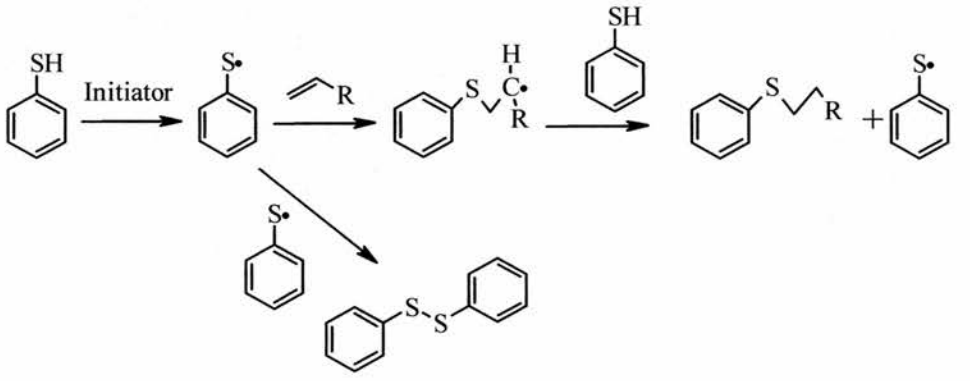
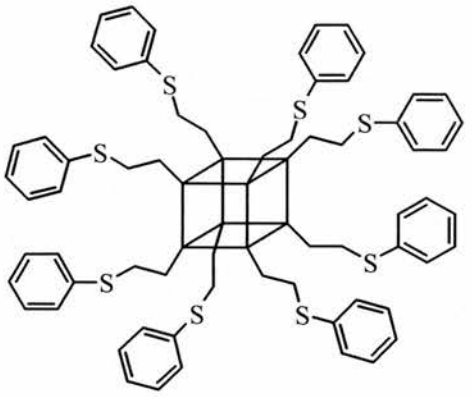


Figure 4.7*. Chain reaction between thiophenol and a vinyl bearing substrate.*[16]

Results and Discussion

Simply refluxing excess thiophenol, vinyl cube and AIBN together was found to produce a POSS bearing thiol groups with aromatic rings at their extremities (**52**). Resonances due to vinyl groups do not appear in the ^{1}H NMR spectra of the purified product, indicating that most, if not all, the groups attached to the cubes reacted. The presence of CH_2 peaks and aromatic resonances in addition to the FTIR data suggest that the reaction proceeded as intended forming the thiol-functionalised POSS 1,3,5,7,9,11,13,15-Octakis{thiophene}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]-octasiloxane $[SiO_{3/2}C_2H_4SC_6H_5]_8$ (**52**) (***Figure 4.8***).



52

***Figure 4.8**. Product **52** from thiophenol/vinyl silsesquioxane reaction.*

Full characterisation **52** has not been possible due to unsatisfactory microanalysis data which may have been due to incomplete reaction or the inherent instability of the molecule. Shortly after purification, the product begins to decompose, reverting back to thiophenol and vinyl functionalised POSS even when kept below room temperature under an inert atmosphere.

Excess thiophenol was used in these experiments to allow it to be used as both reactant and solvent permitting a reaction temperature of 169 °C to be employed but as a consequence, a quantity of diphenyl-disulphide was formed. It was found that the properties of the disulphide are very similar to those of **52** and only a slight separation was achieved during chromatography. This meant that the raw product generally had to be passed through several columns to ensure complete removal of the disulphide. In an effort to minimised the quantity of disulfide by-product formed, attempts were made to perform the reaction in cylclohexane using stoichiometric quantities of reactants after reports of radical reactions of phosphines initiated by AIBN occurring with **7** in this solvent.[26] As well as reducing the amount of disulphide by-product formed during the reaction, the success of this reaction would also demonstrate that it

could be possible to use solvents in reactions of 4-aminothiophenol to allow simple control of the reaction temperature.

This reaction did not go to completion and even with an excess of thiophenol in solution only partial reaction was observed. Although there was the possibility of side reactions occurring through radical generation from the solvent, the reaction was also performed using toluene and then mesitylene as solvents to give reaction temperatures of 110 and 165 °C respectively. Again, only partial reaction was observed but it was not possible to determine if the low reaction yield was due to dilution of the radical species, quenching of the reaction by the solvent, the reaction temperature or a combination of all three. To remedy this, the reaction was repeated with no solvent and the heat being supplied by a silicone oil bath at 110 °C but this did not produce a high yield of modified vinyl groups. Thiol radical reactions with vinylsilanes have been documented as occurring at or below 110 °C which suggests that oxygen linked to vinylsilanes deactivates the vinyl group to radical reaction and a high reaction temperature is required to compensate.[27]

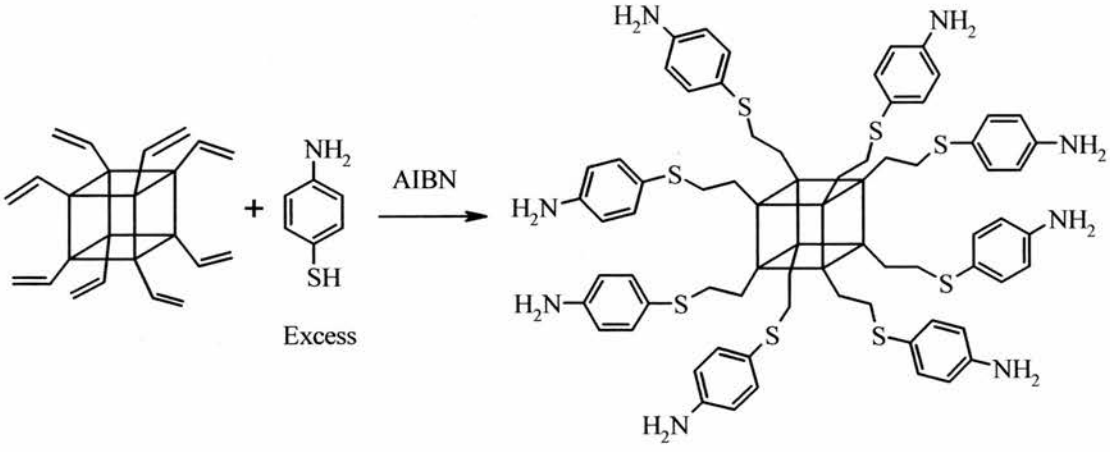
At high temperatures, the reaction of thiophenol with **7** has a much lower yield over a reaction period of several hours than an equivalent reaction of thiophenol with triethoxyvinylsilane. Sheshadri and Haupt observed that if they employed a temperature which was too low, no reaction occurred between the silanes and thiols used in their studies with yields of less than 90% being obtained even when the reaction temperature was 169 °C.[23] Following the extended reaction period of 10 days used in this project, no vinyl groups are detectable by NMR indicating a yield approaching 100% which does not appear to have been reported for any other vinyl

silane/thiol reaction. A reaction time of only 3 hours, results in a barely detectable number of the vinyl groups reacting but the yield can be increased by using longer reaction times with complete reaction being observed after reflux for 10 days.

Radical reactions are generally rapid as evidenced by Sheshadri and Haupt's reactions which were complete in only 10 hours. This suggested that the reaction mechanism was not based on radical formation and an experiment was run without initiator being added to the reaction mixture. An insignificant proportion of the vinyl groups reacted indicating that an initiator is required to generate radicals to at least begin the reaction. It appears that a component of the reaction mixture continues to generate radicals as a non-radical active species would be likely to produce a mixture of α and β products but only reaction at the α carbon was observed. Since the reaction occurring in the absence of an initiator is essentially negligible, the radical source cannot be the thiophenol but may be the disulphide formed by thiophenol radicals combining.

Diphenyl-disulphide is known to undergo homolytic cleavage through the sulphur-sulphur bond when exposed to UV or near-UV light at relatively low temperatures.[28] Although none of the reactions were performed under unadulterated UV light, they were all exposed to daylight and the reaction temperature of 169 °C may have been sufficient to cause disulphide cleavage. This would have produced a steady stream of radicals, which could then react with the vinyl groups giving complete reaction after 10 days.

Once it had been demonstrated that thiophenol could be induced to react with a vinyl functionalised POSS, an attempt was made to repeat the reaction using 4-aminothiophenol. Heating the reaction mixture at 170 °C produced a dark brown reaction tar that appears to be a homogeneous material. Although excess 4-aminothiophenol was used, no unreacted material could be isolated from the reaction mixture. NMR studies of the raw product gave very unclear results with many unidentified peaks appearing in the ^{1}H and ^{13}C NMR spectra, but no vinyl resonances were observed in either. Filtration, distillation, chromatography and acid/base washes all failed to isolate any of the expected product (***Figure 4.9***), disulphide or unreacted starting materials. There is, however, indication in the NMR spectra that an ethyl linkage has been formed during the reaction and resonances which could be associated with this group are present in positions consistent with those observed for **52**.



61

Figure 4.9. *Possible scheme for the AIBN initiated reaction of 4-aminothiophenol with 7 (**61**).*

As one of the major by-products in the reaction mixture was expected to be a disulphide, attempts were made to reduce this disulphide component back to 4-

aminothiophenol to allow it to be removed under reduced pressure to assist in the purification of the sample. The attempted reduction[29] produced only a small volume of 4-aminothiophenol and did little to change the nature of the product mix, suggesting that there may be very little of the expected disulphide present.

In an effort to avoid producing tar-like product mixtures, experiments were performed using toluene and mesitylene as solvents, but as in the thiophenol experiments, the use of solvents only resulted in a partial reaction. The NMR data from the toluene experiment suggested that only an average of 1 to 2 vinyl groups per cube reacted whilst those obtained from the mesitylene experiment indicated a slightly higher yield. In both cases, the was no indication that any S-H groups were left intact on completion of the experiments indicating complete reaction of the thiol but with substrates other than the vinyl components of the POSS.

Excess 4-aminothiopheniol was used throughout these experiments and it was expected that some of this excess would remain intact but as none has been detected, side reactions must be occurring. Since the reduction reactions, employed to break the sulphur-sulphur bond of any disulphides present, produced no discernible effect it is likely that the side reactions are occurring between molecules of 4-aminothiophenol and thiol groups bound to the POSS. This would produce a high molecular weight product with properties that would be very similar to those observed in the products of these reactions.

Conclusions

It has been demonstrated here that aromatic thiyl radicals can react with vinyl functionalised POSS to produce thiol bearing POSS. Simply refluxing excess thiophenol, vinyl-functionalised POSS and AIBN together was found to be an effective way to produce a POSS bearing thiol groups with aromatic rings at their extremities although purification of the product was difficult due to the disulphide by-product.

High yields were obtained from the thiophenol/vinyl cube reaction, higher in fact than those observed when triethoxyvinylsilane is used as the vinyl source. This appears to be due to the high reaction temperature used and the extended reaction time of 10 days allowing the diphenyl-disulphide by-product to break down and react with the cube (***Figure 4.10***). The tendency for the product to decompose does indicate however that this type of thiol bearing POSS will probably not be suitable for use in porous materials as their structure would almost certainly collapse in a relatively short time as the groups linking the cubes fell apart.

Further investigation of this type of reaction may be successful if some means of stabilising the carbon-sulphur bond can be introduced, possibly through the careful selection of groups attached to the aromatic ring. It was thought that this may be a lengthy if not impossible task and time would be better spent developing alternative routes to produce POSS with stable moieties suitable for self-assembly.

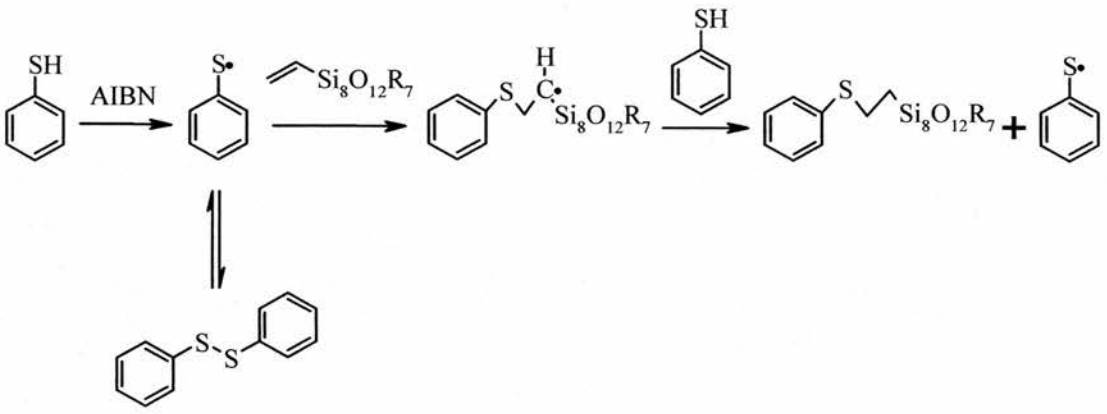


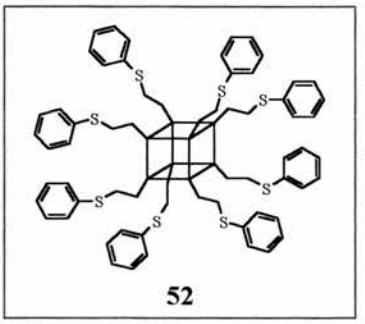
Figure 4.10. *Proposed scheme for reaction between a vinyl functionalised POSS (where R can be vinyl or thiol groups) and thiophenol with AIBN initiator.*

Experimental

General. Thiophenol (Lancaster), 4-aminothiophenol (Aldrich), AIBN (Koch-Light Laboratories Ltd), mesitylene (Aldrich) and argon (BOC) were used as supplied. Cyclohexane (Ultrafine Ltd) and xylene (Fisher) were dried with calcium hydride (Aldrich) and distilled from sodium prior to use. Toluene (Ultrafine Ltd) was distilled from benzophenone prior to use. Information on the analytical equipment and techniques is provided in **Appendix B**.

Preparation of $[SiO_{3/2}C_2H_3]_8$ (7). Prepared as in **Chapter 2** page 94.

Preparation of $[SiO_{3/2}C_2H_4SC_6H_5]_8$ (52). Thiophenol (25.32 g, 230 mmol) was added to a dry mixture of **7** (0.300 g, 0.47 mmol) and AIBN (0.0031 g, 0.019 mmol) under an argon atmosphere. The resultant mixture was then refluxed with constant stirring for 10 days. After cooling, the excess thiophenol was removed under reduced pressure and the product was purified by column chromatography (silica gel 220-440 mesh, diethyl ether elutant) to afford a green oil (0.31 g, 44 %). ^{1}H NMR ($CDCl_3$) δ 7.10-7.42 (m, C**H**, 40H), 3.19 (t, J_{HH}=8.0 Hz, C**H**$_2$, 16H), 1.33 (t, J_{HH}=8.0 Hz, C**H**$_2$, 16H). ^{13}C NMR ($CDCl_3$) δ 136.21 (S-**C**H), 129.22 (**C**H), 129.11 (**C**H), 126.14 (**C**H), 27.97 (S-**C**H_2-CH_2), 12.63 (Si-**C**H_2-CH_2). ν_{max}/cm^{-1} (NaCl/$CDCl_3$) 3059 (w, CH), 3005 (w, CH), 2921 (w, CH), 1601 (w), 1279 (m, Si-C), 1114 (s, Si-O), 1043 (m), 1030 (m), 820 (m, aryl CH), 691 (m, C-S). No Satisfactory CHN microanalysis was obtained.



52

Attempted preparation of 52 over 3 hours. (53). The reaction used to prepare **52** was repeated but over 3 hours using 8.08 g (73 mmol) thiophenol, 0.100 g (0.16 mmol) **7** and 0.0010 g (0.006 mmol) AIBN to yield a viscous green oil (0.16 g). ^{1}H NMR ($CDCl_3$) δ 7.56 (m, C**H**, disulphide), 7.09-7.45 (m, C**H**, disulphide and product), 6.12 - 5.81 (m, C**H**=C**H**$_2$, 23H), 3.19 (t, J_{HH}=8.0 Hz, C**H**$_2$, 0.6H), 1.34 (t, J_{HH}=8.0 Hz, C**H**$_2$, 0.5H). ^{13}C NMR ($CDCl_3$) δ 137.06 (S-**C**, disulphide), 137.02 (-C=CH_2), 136.20 (S-**C**H), 129.31 (**C**H), 129.21 (**C**H), 129.13 (**C**H), 128.69 (-C=CH_2), 127.53 (**C**H, disulphide), 127.19 (**C**H, disulphide),126.12 (**C**H), 27.96 (S-**C**H_2-CH_2), 12.62 (Si-**C**H_2-CH_2).

Attempted preparation of 52 over 1 day. (54). The reaction used to prepare **52** was repeated but over 1 day using 8.12 g (74 mmol) thiophenol, 0.100 g (0.16 mmol) **7** and 0.0010 g (0.006 mmol) AIBN to yield a viscous green oil (0.19 g). ^{1}H NMR ($CDCl_3$) δ 7.57 (m, C**H**, disulphide), 7.10-7.45 (m, C**H**, disulphide and product), 6.14 - 5.80 (m, C**H**=C**H**$_2$, 21.4H), 3.17 (t, J_{HH}=8.0 Hz, C**H**$_2$, 1.9H), 1.34 (t, J_{HH}=8.0 Hz, C**H**$_2$, 1.9H). ^{13}C NMR ($CDCl_3$) δ 137.06 (S-**C**, disulphide), 137.05 (-C=CH_2), 136.19 (S-**C**H), 129.31 (**C**H), 129.23 (**C**H), 129.11 (**C**H), 128.67 (-C=CH_2), 127.55 (**C**H, disulphide), 127.20 (**C**H, disulphide),126.14 (**C**H), 27.97 (S-**C**H_2-CH_2), 12.63 (Si-**C**H_2-CH_2).

Attempted preparation of 52 over 5 days. (55). The reaction used to prepare **52** was repeated but over 5 days using 8.02 g (73 mmol) thiophenol, 0.101 g (0.16 mmol) **7** and 0.0010 g (0.006 mmol) AIBN to yield a viscous green (0.20 g). ^{1}H NMR ($CDCl_3$) δ 7.53 (m, C**H**, disulphide), 7.09-7.40 (m, C**H**, product and disulphide), 6.10 - 5.81 (m, C**H**=C**H**$_2$, 9.1H), 3.19 (t, J_{HH}=8.0 Hz, C**H**$_2$, 9.9H), 1.33 (t, J_{HH}=8.0 Hz, C**H**$_2$, 9.7H). ^{13}C NMR ($CDCl_3$) δ 137.05 (S-**C**, disulphide), 137.01 (-C=CH_2), 136.24 (S-**C**H), 129.32 (**C**H), 129.21 (**C**H), 129.14 (**C**H), 128.68 (-C=CH_2), 127.54 (**C**H, disulphide), 127.19 (**C**H, disulphide),126.12 (**C**H), 27.94 (S-**C**H_2-CH_2), 12.63 (Si-**C**H_2-CH_2).

Attempted preparation of 52 in cyclohexane (56). Thiophenol (0.141g, 1.28 mmol) was added to a solution of **7** (0.101 g, 0.16 mmol) and AIBN (0.0030 g, 0.018 mmol) in dry cyclohexane (10 cm^3) under an argon atmosphere. The resultant solution was refluxed with constant stirring for 10 days and was worked up as before to yield a viscous green oil (0.19 g). ^{1}H NMR ($CDCl_3$) δ 7.56 (m, C**H**, disulphide), 7.10-7.42

(m, C**H**, disulphide and product), 6.22 - 5.86 (m, C**H**=C**H**$_2$, 17.5H), 3.19 (t, J_{HH}=8.0 Hz, C**H**$_2$, 4.3H), 1.33 (t, J_{HH}=8.0 Hz, C**H**$_2$, 4.2H). ^{13}C NMR ($CDCl_3$) δ 137.06 (S-**C**, disulphide), 137.02 (-C=CH_2), 136.21 (S-**C**H), 129.32 (**C**H), 129.22 (**C**H), 129.11 (**C**H), 128.687 (-C=CH_2), 127.54 (**C**H, disulphide), 127.19 (**C**H, disulphide),126.14 (**C**H), 27.97 (S-**C**H_2-CH_2), 12.63 (Si-**C**H_2-CH_2).

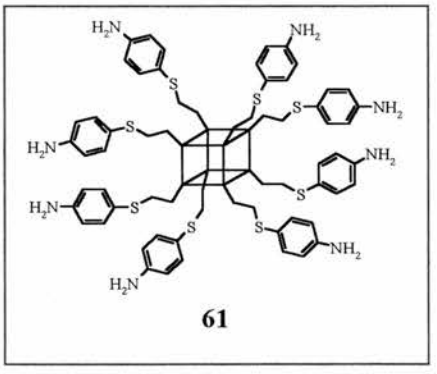
Attempted preparation of 52 in toluene (57). The reaction detailed above was repeated using 0.143 g (1.30 mmol) thiophenol, 0.100 g (0.16 mmol) **7,** 0.0032 g (0.019 mmol) AIBN in dry toluene (10 cm^3) to yield a viscous green oil (0.110 g). ^{1}H NMR ($CDCl_3$) δ 7.10-7.42 (m, C**H**, 40H), 6.14 - 5.82 (m, C**H**=C**H**$_2$, 16.6H), 3.19 (t, J_{HH}=8.0 Hz, C**H**$_2$, 5.0H), 1.33 (t, J_{HH}=8.0 Hz, C**H**$_2$, 4.9H). ^{13}C NMR ($CDCl_3$) δ 137.06 (S-**C**, disulphide), 137.02 (-C=CH_2), 136.21 (S-**C**H), 129.32 (**C**H), 129.22 (**C**H), 129.11 (**C**H), 128.687 (-C=CH_2), 127.54 (**C**H, disulphide), 127.19 (**C**H, disulphide), 126.13 (**C**H), 27.97 (S-**C**H_2-CH_2), 12.63 (Si-**C**H_2-CH_2).

Attempted preparation of 52 in mesitylene (58). The reaction detailed above was repeated using 0.140 g (1.28 mmol) thiophenol, 0.098 g (0.15 mmol) **7,** 0.0031 g (0.019 mmol) AIBN in dry mesitylene (10 cm^3) to yield a viscous green oil (0.13 g). ^{1}H NMR ($CDCl_3$) δ 7.10-7.42 (m, C**H**, 40H), 6.14 - 5.82 (m, C**H**=C**H**$_2$, 20.9H), 3.19 (t, J_{HH}=8.0 Hz, C**H**$_2$, 3.8H), 1.33 (t, J_{HH}=8.0 Hz, C**H**$_2$, 3.6H). ^{13}C NMR ($CDCl_3$) δ 137.06 (S-**C**, disulphide), 137.02 (-C=CH_2), 136.21 (S-**C**H), 129.32 (**C**H), 129.22 (**C**H), 129.11 (**C**H), 128.687 (-C=CH_2), 127.54 (**C**H, disulphide), 127.19 (**C**H, disulphide),126.14 (**C**H), 27.96 (S-**C**H_2-CH_2), 12.63 (Si-**C**H_2-CH_2).

Attempted preparation of 52 with heating by oil bath (59). The reaction used to prepare **57** was repeated at 110 °C in an oil bath using 23.98 g (218 mmol) thiophenol, 0.300 g (0.47 mmol) **7** and 0.0031 g (0.019 mmol) AIBN to yield a viscous green oil (0.44 g). ^{1}H NMR ($CDCl_3$) δ 7.10-7.42 (m, C**H**, 40H), 6.14 - 5.82 (m, C**H**=C**H**$_2$, 13.68H), 3.19 (t, J_{HH}=8.0 Hz, C**H**$_2$, 6.88H), 1.33 (t, J_{HH}=8.0 Hz, C**H**$_2$, 6.88H). ^{13}C NMR ($CDCl_3$) δ 137.02 (-C=CH_2), 136.21 (S-**C**H), 129.22 (**C**H), 129.11 (**C**H), 128.65 (-C=CH_2), 126.14 (**C**H), 27.96 (S-**C**H_2-CH_2), 12.64 (Si-**C**H_2-CH_2).

Attempted preparation of 52 without initiator (60). The reaction used to prepare **52** was repeated without initiator using 25.15 g (210 mmol) thiophenol and 0.300 g (0.47 mmol) **7** to yield a white powder (0.31 g. ^{1}H NMR ($CDCl_3$) δ 7.10-7.40 (m, C**H**, trace), 6.14 - 5.82 (m, C**H**=C**H**$_2$, ~24H), 3.19 (s, C**H**$_2$, trace), 1.32 (s, C**H**$_2$, trace).

Attempted preparation of [$SiO_{3/2}C_2H_4SC_6H_4NH_2$]$_8$ (61). 4-Aminothiophenol (2.210 g, 17.7 mmol) was added to a dry mixture of **7** (0.381 g, 0.60 mmol) and AIBN (0.0100 g, 0.06 mmol) under an argon atmosphere. The resultant mixture was then heated at 170 °C with constant stirring for ten days. After cooling the product mixture was heated under vacuum (100 °C, 0.2 mmHg) and passed through a celite column (dichloromethane elutant) to yield a highly viscous brown tar (2.23 g). TLC (range of solvents) single spot. ^{1}H NMR ($CDCl_3$) δ 7.02-7.53 (m, C-**H**), 6.61-6.43 (m, C-**H**), 3.85 (broad s, N-**H**$_2$), 2.88 (broad s, S-C**H**$_2$-CH_2, 2H), 1.01 (broad s, Si-C**H**$_2$-CH_2, 2H). ^{13}C NMR ($CDCl_3$) δ 148.42, 148.28, 147.92 (**C**-NH_2, product), 147.44 (**C**-NH_2, disulphide), 137.00, 135.43,



61

135.28, 134.97 (**C**H, product), 134.23 (**C**H, disulphide), 133.51, 132.82, 125.43 (S-**C**, disulphide), 125.28 (S-**C**, product), 124.73, 124.07, 122.70, 116.07 (**C**H, product), 115.89. 115.49 (**C**H, disulphide), 115.24, 65.94, 53.75, 31.10 (S-**C**H_2-CH_2), 29.78, 16.33, 12.90 (Si-**C**H_2-CH_2).

Attempted preparation of $[SiO_{3/2}C_2H_4SC_6H_4NH_2]_8$ using toluene (62). The reaction used to prepare product **61** was repeated in refluxing toluene (15 cm^3) using 0.844 g (6.73mmol) 4-aminothiophenol, 0.300 g (0.47 mmol) **7** and 0.0031 g (0.019 mmol) AIBN to yield a viscous brown tar. ^{1}H NMR ($CDCl_3$) δ 7.02-7.53 (m, C**H**, disulphide, product, 4-aminothiophenol), 6.50-6.62 (m, C**H**, disulphide, product, 4-aminothiophenol), 6.13 - 5.80 (m, C**H**=C$\mathbf{H}_2$, 15.1H), 3.86 (broad s, N$\mathbf{H}_2$), 2.88 (broad s, S-C$\mathbf{H}_2$-CH_2, 2.7H), 1.05 (broad s, Si-C$\mathbf{H}_2$-CH_2, 2.7H).

Attempted preparation of $[SiO_{3/2}C_2H_4SC_6H_4NH_2]_8$ using mesitylene (63). The reaction used to prepare product **61** was repeated in refluxing mesitylene (5 cm^3) using 0.341 g (2.72 mmol) 4-aminothiophenol, 0.120 g (0.19 mmol) **7** and 0.0020 g (0.012 mmol) AIBN to yield a viscous brown tar (0.12 g). ^{1}H NMR ($CDCl_3$) δ 7.02-7.53 (m, C**H**, disulphide, product, 4-aminothiophenol), 6.51-6.61 (m, C**H**, disulphide, product, 4-aminothiophenol), 6.14 - 5.82 (m, C**H**=C$\mathbf{H}_2$, 19.0H), 3.85 (broad s, N$\mathbf{H}_2$), 2.88 (broad s, S-C$\mathbf{H}_2$-CH_2, 3.4H), 1.07 (broad s, Si-C$\mathbf{H}_2$-CH_2, 3.4H).

Attempted reduction of disulphide by-product produced with 61 (64). Triphenyl phosphine (0.36 g, 1.37 mmol) was added to a portion of **61** (0.35 g) and 1 drop of concentrated HCl in dioxane (10 cm^3) and water (3 cm^3) under a nitrogen atmosphere. The resultant mixture was heated for 1 hour at 40 °C with constant stirring. The

solvent was removed under reduced pressure and the solid extracted into dichloromethane which was dried over magnesium sulphate with thorough mixing. The product mixture was subjected to short path distillation (100 C, 0.2 mmHg) to remove the 4-aminothiophenol produced by the reduction reaction (0.09 g). Once the thiol had been removed, a dark brown tar remained (0.27 g). ^{1}H NMR ($CDCl_3$) δ 7.02-7.53 (m, C-**H**), 6.61-6.43 (m, C-**H**), 4.35 (m), 3.85 (broad s, N**H**$_2$), 3.20 (m), 2.88 (broad s, S-C**H**$_2$-CH$_2$, 2H), 2.49 (m), 2.00 (m), 1.56 (m), 1.23 (m), 1.01 (broad s, Si-C**H**$_2$-CH$_2$, 2H), 0.24 (s).

4.5 General Conclusions

None of the synthetic methods investigated here proved suitable for the preparation of self-assembling molecular building blocks.

The Heck-type arylation shows promise as a route to functionalised POSS, but it is expected that this method of functionalisation will never generate very high yields. The yield of the palladium (II) chloride reaction between iodotoluene and octavinyl silsesquioxane **7** is one third of that obtained when iodotoluene is combined with trimethylvinylsilane suggesting that more efficient catalyst systems will only marginally improve the yield of reactions involving vinyl POSS.

As with the Heck-type arylation, the yields obtained from the Gabriel synthesis experiments are not high enough to allow POSS suitable for the preparation of well-ordered materials to be synthesised. However, despite being too low to be

useful, the yield from this reaction is much higher than that observed for the Heck-type arylation.

The reaction of thiophenol with octavinyl silsesquioxane **7** has proved to be high yielding but the product is unstable and decomposes upon isolation. Furthermore, the introduction of an extra functional group to the thiol in the form of an amine results in the formation of a thick reaction tar. The instability observed in the products of these experiments indicates that molecules of this type are not suitable for the preparation of porous materials but the experiments demonstrate that vinyl groups bound to POSS can react with free radicals. This could mean that further studies using non-thiyl radical species may produce useful molecules with a greater degree of stability.

Although they do not meet the requirements of this project, the synthetic methods described above may prove useful in other areas of research. Both the Heck-type arylation and the Gabriel synthesis could, for example, be used in the preparation of hard blocks for high performance polymers. The POSS used in this type of application are not bound to the polymer through all their functional groups and therefore do not need to be highly functionalised. Where long term stability and purity are not critical, applications requiring highly functionalised POSS could be satisified using POSS functionalised using thiyl radicals.

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Chapter 5 POSS-Based Copolymers

5.1 General Introduction

It was initially thought by our group that copolymerising POSS functionalised with non-rigid groups would simply produce nonporous materials, a view apparently confirmed by studies carried out by Hoebbel *et al.*[1] Harrison *et al*[2] then later Zhang and co-workers[3] demonstrated that hydrosilylative copolymerisation of POSS could, however, be used to produce porous solids (***Figure 5.1***). As this approach does not tightly control the orientation of the POSS molecules the porous structure of the materials produced have a wide variety of pore sizes in the micro and mesopore regions. Despite the lack of an obvious control mechanism, these reactions produce repeatable results with respect to surface area and porosity indicating that they are not as random as they first appear. Indeed, Zhang *et al* speculated that there was some order being introduced into these materials by a 'zipping' action as POSS are bound to the structure and the reaction becomes almost a self-assembly process. [3]

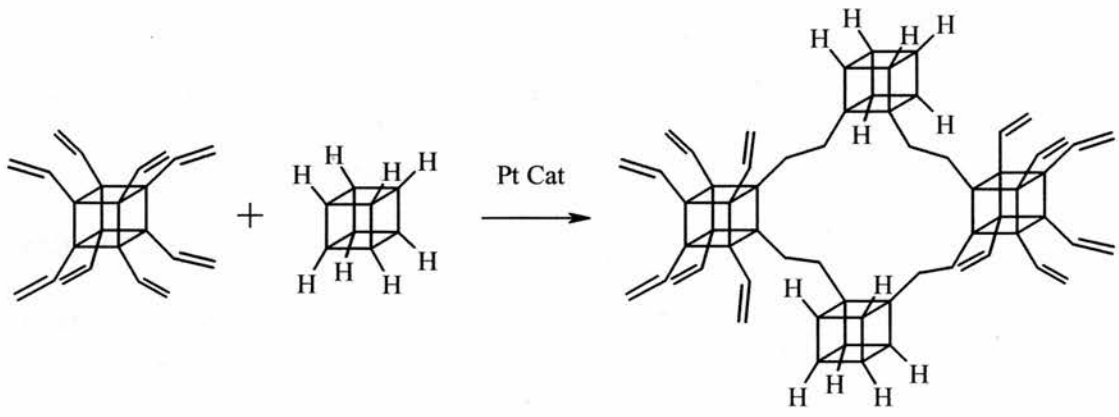


Figure 5.1. *Example of a possible pore opening formed by copolymerised POSS.*

This type of compound is non-crystalline and lacks a well-ordered structure but it was hoped that by investigating a range of copolymers some insight might be gained into the effect of different POSS functional groups on porosity. The viability of preparing porous materials from building blocks bearing non-rigid functional groups was of particular interest as this has implications for the preparation of POSS for use in co-ordination or hydrogen bonded networks. Many of the problems encountered in the synthesis of functionalised POSS are due to the electron-withdrawing effect of the silicon-oxygen core on the functional groups attached to the POSS. By placing several atoms between the core and the functional group being modified, this effect could be reduced or inhibited making it easier to perform synthetic manipulations on the functional groups to yield useful POSS.

Despite the lack of order in POSS-based copolymers and the range of pore sizes within them, they may still make useful starting points for the preparation of catalytic systems and a preliminary investigation of this was performed as part of this project. Due to the steric and geometric constraints created as the copolymers form, they tend to contain a number of unreacted functional groups when copolymerisation is complete. It may therefore be possible to fix catalytic sites/moieties into these materials by simple synthetic manipulation of these groups, using the pore structure to gain access to them. Although this type of experimentation could be viewed as being within the scope of this project, this topic is currently being investigated elsewhere within our research group and will not be considered here.

Another possible means by which catalysts could be prepared from POSS-based copolymers is the incorporation of metals into the POSS structure by acid or

base cleavage.[4, 5, 6] As this technique had only been used on discrete POSS molecules it was not clear if the steric constraints on cubes within a polymer would hinder cleavage, encourage the reverse reaction or if the technique would even be effective inside the polymer. Although base cleavage directly forms silanol groups ideal for reaction with metal complexes,[8] it was anticipated that cleavage using triflic acid would be as effective and that the ditriflate units formed would be relatively stable. As it was only the feasibility of the cleavage process in copolymers being studied here, triflic acid was selected for these experiments as a stable product for analysis was required rather than a reactive species ready for further reaction.

As only a limited number of porous copolymers had previously been prepared from POSS, attempts were made to produce new copolymers from a variety of precursors. By using different POSS and linking units, it was expected that a range of materials would be produced for the cleavage experiments and that correlation could be made between porosity and types of precursor used. Silicate precursors can be used to prepare porous copolymers in the same manner as silsesquioxanes[3] but unlike silsesquioxane-based copolymers, they contain sub-units linked through one or more silicon-oxygen bonds. As the proposed triflic acid cleavage reaction operated by cleaving silicon-oxygen bonds, it was considered prudent to apply this reaction only to silsesquioxane-based copolymers and silicate-based copolymers were not prepared. This allowed the relationship between porosity, functional group and reaction conditions to be investigated in phase one of this study and the cleavage of the porous materials generated to be investigated in phase two. Successful results could then be followed up in subsequent research projects with a view to preparing a catalytically active materials.

5.2 Preparation of Hydrosilylativiely Copolymerised POSS

Introduction

A variety of copolymers have been prepared from both POSS-POSS mixtures[2, 3] and POSS-spacer mixtures.[1, 8, 9, 10] Many of these inorganic/organic hybrids have been formed from silicate precursors of the general formula $[ROSiO_{3/2}]_8$ resulting in networked cubes linked by bridges containing silicon and oxygen as well as carbon and hydrogen. Although these materials have been well documented, the presence of silicon-oxygen elements between the cube structures in these copolymers was expected to hamper attempts to use acid or base cleavage to introduce catalytic sites into them. The controlled cleavage of POSS is known to selectively open elements of POSS cubes, but it was expected that silicon-oxygen bridges would provide another point of attack which would result in the destruction of the macro structure of the material. No silicate precursors were therefore used in any of these experiments but it was still possible to prepare a variety of materials, most of them previously unreported.

Several spacer motifs had previously been used in silsesquioxane and silicate copolymers but these were non-aromatic or contained flexible units and produced low surface area or non-porous polymers.[1, 8, 10] The introduction of aromatic systems into sol-gel reactions dramatically increases the surface area of the solids formed by them and it was expected that the incorporation of such groups into POSS copolymers would also produce materials with very high surface areas.[11] To introduce aromatic rings into the copolymers, it was decided that the less synthetically demanding route

would be to use one species of POSS and to combine it with a spacer functionalised with appropriate groups.

A range of precursors suitable for use in silsesquioxane based copolymers had already been created by various researchers allowing work to proceed without the development of new molecules (***Figure 5.2***). By using a range of POSS molecules and spacers in various combinations a range of new copolymers could be prepared and attempts could then be made to correlate their surface areas with the nature of the functional groups involved.

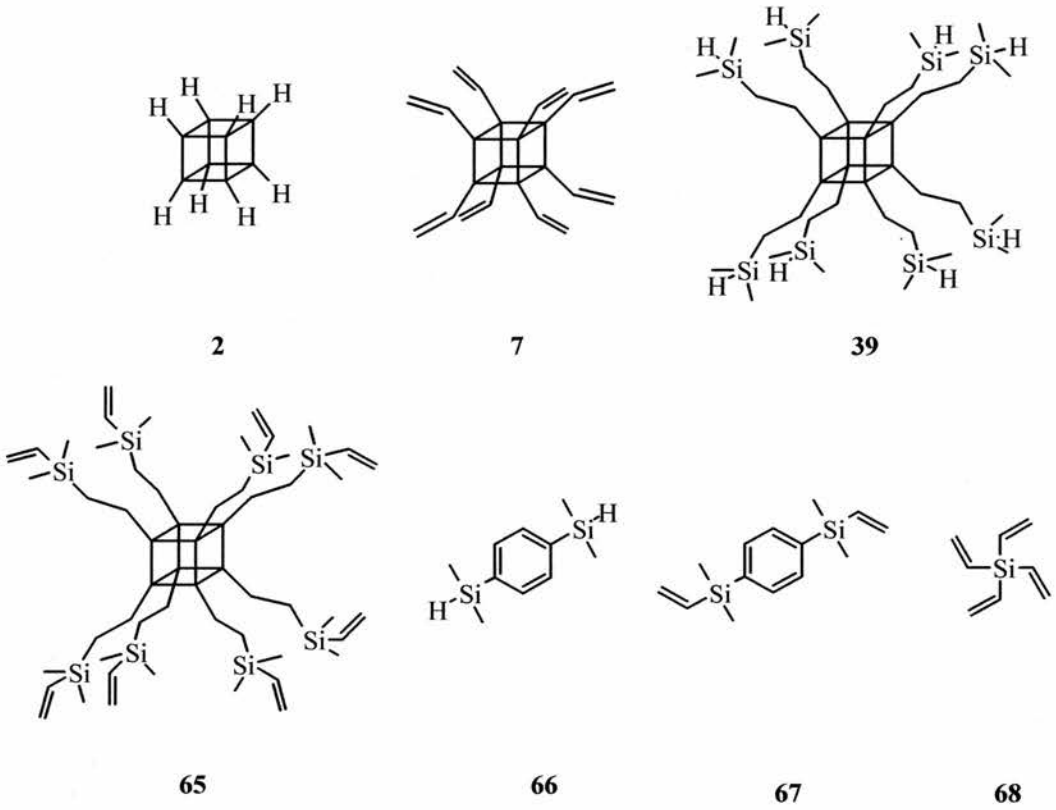


Figure 5.2. POSS cubes $[SiO_{3/2}H]_8$ (**2**),[12] $[SiO_{3/2}C_2H_3]_8$ (**7**),[13] $[SiO_{3/2}C_2H_4Si(CH_3)_2H]_8$ (**39**),[14] $[SiO_{3/2}C_2H_4Si(CH_3)_2C_2H_3]_8$ (**65**)[14] and spacers bis-dimethylsilylbenzene (**66**),[15] bis-vinyldimethylsilylbenzene (**67**), tetravinylsilane (**68**) used for copolymerisation. Note: **68** is commercially available but was given a product number for convenience.

Initially, a previously reported copolymer was prepared from **2** and **7** to ensure that the techniques used in this project were equivalent to those used elsewhere allowing general comparisons to be made with other studies.[2, 3] Accurate accounts of reaction conditions, in particular concentrations, were not always given by other researchers however, which prevented detailed comparisons being made across these experiments. For the purposes of the work carried out here, the concentration of the POSS cubes was kept constant throughout the experiments to keep the opportunity for contact between cubes and other reaction elements constant.

Results and Discussion

Once a methodology had been established, POSS-based copolymers were prepared using the full range of precursors. The reaction conditions and catalyst were varied for each pair of precursors and a range of copolymers were produced, some porous, many non-porous. These materials were initially investigated using basic surface-area measurements and FTIR spectroscopy with solid-state NMR and more detailed surface-area studies then being applied to key copolymers.

The surface-area measurements allowed identification of copolymers with porous structures and provided information on the nature of those structures. Multipoint BET measurements were taken to determine the mean surface area of copolymer samples with porous materials then being subjected to more rigorous analysis through full absorption/desorption isotherms. Both the multipoint BET and

full isotherm surface-area measurements were performed through the St Andrews University CATs service.

Transmission FTIR spectroscopy was a convenient method by which the composition of the copolymers could be assessed. In particular, key absorptions such as those due to Si-H groups could be identified or their absences noted, giving an insight into the nature of the copolymerisation process. The FTIR spectra were obtained from KBr disks prepared using ground samples of dry polymer but it was found to be extremely difficult to get a good dispersion of the copolymers throughout the disks. It is therefore recommended that the application of non-transmission techniques such as DRIFTs should be investigated in future studies on these types of copolymer.

Due to the expense involved and time available during the course of this project, only copolymers of particular interest were subjected to solid-state NMR. Both ^{13}C and ^{29}Si spectra were obtained for the copolymers studied in this way and these yielded information on the linkages in both porous and non-porous copolymers. All solid state NMR spectra were gathered using the EPSRC Solid-State NMR Service based at Durham University.

Powder X-ray diffraction was employed in an attempt to investigate any order within the structure of the copolymers and differences between porous and non-porous samples. Although a degree of order was apparent in the XRD data, the technique could not offer enough resolution in the data sets to allow it to be used as anything other than a high-level investigative tool.

To simplify presentation of the experimental results, the copolymers have been divided into 7 classes based on their constituent POSS and spacer units (***Figure 5.3***). A summary table of the principle results for each copolymer is presented after the entries for individual polymer classes.

Copolymer Class	Component 1	Component 2
A	POSS **2**	POSS **7**
B	POSS **7**	POSS **39**
C	POSS **39**	POSS **65**
D	POSS **2**	Spacer **67**
E	POSS **7**	Spacer **66**
F	POSS **39**	Spacer **67**
G	POSS **2**	Spacer **68**

Figure 5.3. *Copolymer classes based on their constituent components.*

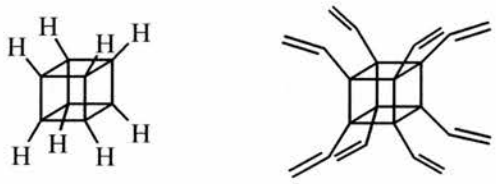
Results for Individual Copolymers

Note: The surface areas stated in this section are for the first repeatable experiment that prepared the copolymer.

*Copolymer class **A**.*

Repeating the experiment described by Harrison and Kannengiesser[2] where POSS **2** was hydrosilylated with POSS **7** (***Figure 5.4***) using chloroplatinic acid failed to produce a copolymer. Analysis of the reaction mixture indicated the presence of the

starting materials and a trace quantity of ethyl groups indicating that almost no hydrosilylation had occurred. Repeating the experiment at room temperature in the manner described by Zhang *et al* [3] using 0.01 mol% and then 0.10 mol% platinum (dvs) produced glassy copolymers **A2** and **A3**, but neither of these materials were found to be porous. By using 0.10 mol% platinum (dvs) and raising the reaction temperature to 80 °C, glassy copolymer **A4** was prepared. This material has a surface area of 676 $m^{-1}g^2$ with 80% cross linking, properties similar to those found in the equivalent material prepared by Zhang *et al.*[3]

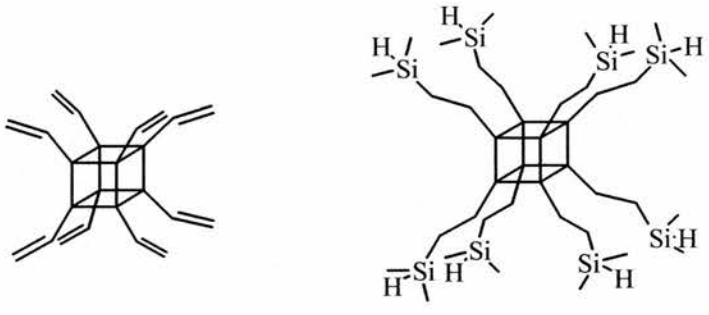


2 **7**

***Figure 5.4**. Precursors 2 and 7 used to prepare class A copolymers.*

These results indicate that, despite attempts to implement reported synthetic methodologies, there is a slight difference between the methodology employed in this study and that employed in other studies although the products are very similar. Once it had been established that **A4** had properties similar to those of previously reported copolymers, attempts were made to prepare several new copolymers.

*Copolymer class **B**.*



7 39

***Figure 5.5.** Precursors 7 and 39 used to prepare class **B** copolymers.*

Hydrosilylating POSS **7** with POSS **39** (***Figure 5.5***) at 80 °C with 0.10 mol% platinum (dvs) produced copolymer **B6**, a glassy porous material with a surface area of 569 m^2g^{-1} and an average pore diameter in the region of 30 Å.

The ^{29}Si and ^{13}C NMR spectra indicate that approximately 85% of the functional groups present in the material have reacted. The unreacted silicon hydride and vinyl groups were detected in both the NMR and FTIR data sets confirming that the material is not completely cross-linked. Repeating the reaction with higher catalyst concentrations of 0.20 mol% and 0.50 mol% produced copolymers **B7** and **B8** respectively. The rate of gelation observed for these copolymers was slightly higher than that observed for **B6** but there was no increase in surface area of the dried copolymers relative to **B6**.

Reactions at room temperature with various catalyst concentrations produced copolymers **B1**, **B2** and **B3** while heating at 80 °C with a catalyst concentration of

0.01 mol% produced **B4**, but on drying these materials were found to be non-porous. The degree of cross linking in these samples was much higher than that observed in the porous samples with the NMR data indicating that approximately 95% of the functional groups have reacted in the non-porous samples. This higher degree of cross-linking was confirmed by a reduction in the magnitude of the silicon hydride and vinyl absorptions in the FTIR spectra of these samples. Reaction at 80 °C with 0.05 mol% platinum (dvs) produced a material (**B5**) with properties lying between those of **B4** and **B6**.

PXRD patterns were gathered from the non-porous materials to allow comparison with those obtained from the porous samples but despite the higher level of cross-linking (***Figure 5.6***), there was no discernible difference between the data sets. This indicates that although there is an obvious physical difference between the porous and non-porous materials, the difference in internal structure is subtle enough to escape detection by the type of XRD employed.

This particular class of copolymer was well studied with over 20 porous samples being prepared between this study and an undergraduate project[16] with individual copolymer types offering a high degree of consistency in the observed properties for both the porous and non-porous sample types. This indicates that although the actual copolymerisation process is not strictly controlled, the mechanism by which it operates produces a similar effect in each reaction possibly hinting at the "self-assembly" suggested by Zhang *et al.*[3]

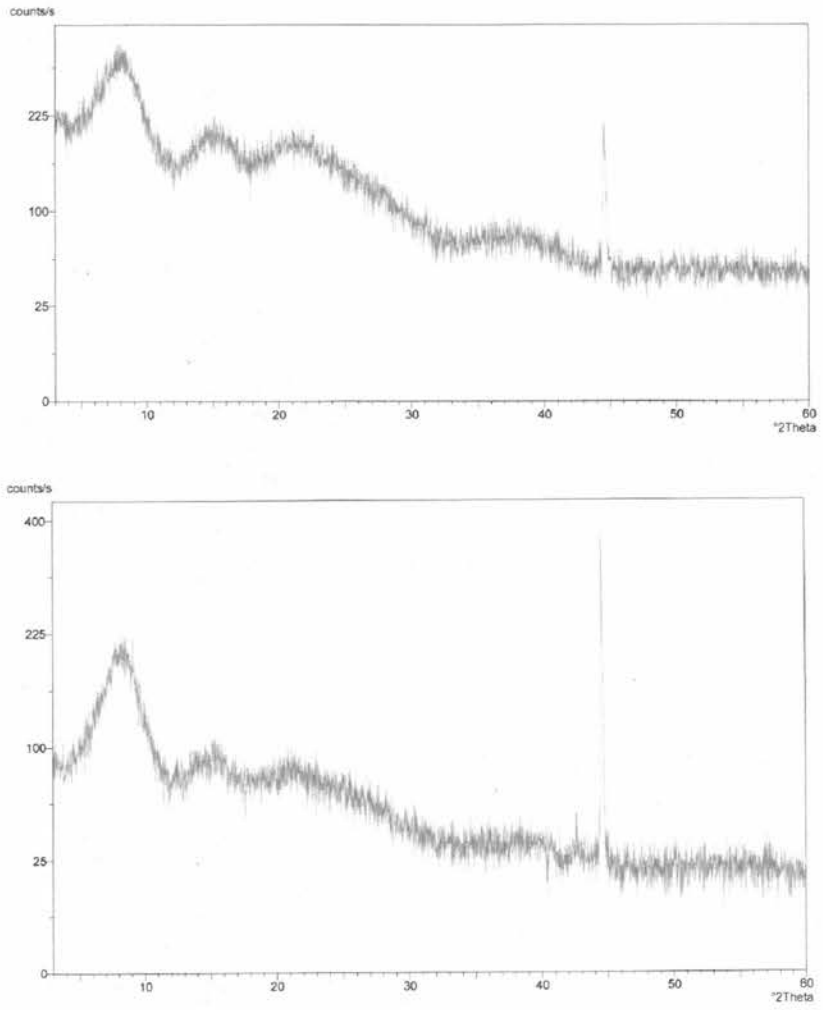
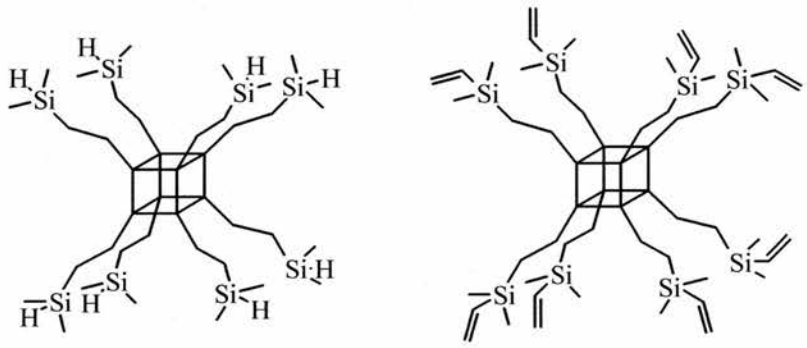


Figure 5.6. *Powder XRD patterns obtained from porous copolymer* ***B6*** *(top) and non-porous copolymer* ***B3*** *(bottom). It should be noted that the sharp peak at 44.3 is due to the sample plate and not the sample itself.*

Copolymers class ***C****.*

Hydrosilylating POSS **39** and POSS **65** (***Figure 5.7***) at room temperature produced **C1**, a glassy non-porous copolymer within 30 minutes of adding the catalyst. ^{29}Si and ^{13}C NMR indicate almost 100% cross linking with FTIR spectroscopy confirming the lack of silicon hydride groups. This is not surprising given the length of the functional groups combined with their flexibility would be

expected to allow folding to produce a dense phase and/or structure inter-penetration. The length and flexibility of the groups would also allow them to sweep a large volume before reaction allowing them to quickly connect with other groups resulting in the rapid gelation observed.



39 **65**

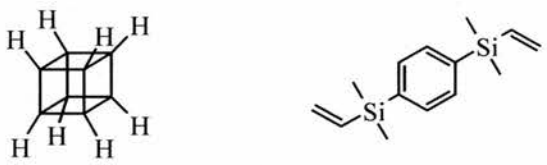
Figure 5.7. *Precursors **39** and **65** used to prepare class **C** copolymer.*

Powder pattern XRD indicates that, as for the **B** class copolymers, a degree of order is present in the copolymer structure but the material is not well defined. Although detailed analysis of the XRD data cannot be performed, the presence of additional broad peaks not present in the data set of the **B** class copolymers indicate a difference in the structures of these materials. Given that the material is non-porous, it can be concluded that the XRD data gives and indication of the structure within the material as opposed to pores.

The preparation of POSS **65** was found to be extremely difficult with only sufficient material being prepared to allow one attempt at the copolymerisation reaction. It was not therefore possible to repeat the experiment at 80 °C to determine

if porous material can be prepared from precursors **39** and **65** or if **C1** is a representive sample of this class of copolymer.

*Copolymers class **D**.*



2 **67**

***Figure 5.8.** Precursors **2** and **67** used to prepare class **D** copolymer.*

Hydrosilylation of POSS **2** and spacer **67** (***Figure 5.8***) at room temperature only produced one copolymer, **D1**. It took 6 weeks for the gel to form with a catalyst concentration of 0.10 mol % and this material was only successfully prepared once with all subsequent reactions under similar conditions failing to produce any gels. Catalyst concentrations below 0.10 mol% at room temperature failed to produce polymers over a similar period of time as did increasing the catalyst concentration to 0.50 mol% and heating the reaction mixture at 80 °C for 1 week.

Analysis of the failed reaction mixtures by NMR revealed that only unreacted **2** and **67** were present in the reaction mixture with a trace quantity ethyl groups, presumably from small scale reactions. The reaction conditions employed can readily produce the other copolymers studied in this project which suggests that the problem must lie with this pair of precursors. Given that POSS **7** with its steric bulk can combine with **2** to produce copolymers, it can be assumed that steric hindrance does not prevent reaction as **67** is much smaller than this POSS. Both precursors can be

hydrosilylated to other molecules, as evidenced by the preparation of the other copolymers although this is not the case when they are combined. This suggests that both of these molecules do not interact well with the catalyst but that this is off set by the other reactants in the successful copolymerisation reactions.

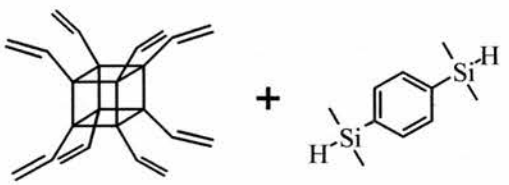
When dried, copolymer **D1** is recovered as small platelets which are attracted to statically charged bodies. The material is non-porous and FTIR spectroscopy indicates that the hydrosilylation reaction has been high yielding as there are no major absorption peaks for Si-H or vinyl groups. This high yield could be due to the large envelope that partially reacted **67** (partially as in one end bound to a POSS cube) can sweep, flexibility in the ethyl linkages between the ring system and the POSS or interpenetration of the copolymer structure as it forms. As **D1** formed over 6 weeks there would have been ample time for any or all of these factors to influence the outcome of the reaction.

As only one copolymer was prepared from a number of attempts, it cannot be viewed as a representative example of copolymerised **2** and **67** and no NMR or PXRD data were therefore collected for this sample.

*Copolymers class **E**.*

Hydrosilylation of POSS **7** and spacer **66** (***Figure 5.9***) at room temperature with catalyst concentrations of 0.01, 0.05 and 0.10 mol % generated copolymers **E1**, **E2** and **E3**. As with copolymer **D1**, these materials are not glassy solids but take the

form of small platelets when dried. Unlike copolymer **D1**, the reactions which formed **E1**, **E2** and **E3** took less than one hour and were found to be irreproducible.



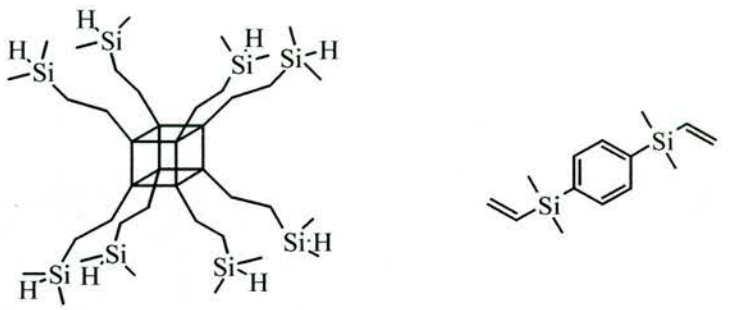
7 **66**

Figure 5.9. *Precursors 7 and* ***66*** *used to prepare class* ***E*** *copolymer.*

These copolymers are non-porous despite the presence of aromatic ring systems of **66** and the dimethylsilane groups attached to it. Using a catalyst concentration of 0.10 mol% and raising the reaction temperature to 80 °C causes a more rapid reaction which takes less than 15 minutes to form copolymer **E4** but this material is also non-porous. As consistent surface area and FTIR results were obtained for all four copolymers, only one sample, **E4**, was investigated further through ^{29}Si NMR, ^{13}C NMR and XRD.

As with the other non-porous copolymer samples, XRD indicates the presence of structures which cannot be attributed to pores. Both the NMR and IR data indicate a high yield from the hydrosilylation reaction with close to 100% of the functional groups reacting. Only trace quantities of vinyl and Si-H groups are present in the NMR spectra while these groups are not apparent in the FTIR data.

*Copolymers class **F**.*



39 **67**

***Figure 5.10.** Precursors **39** and **67** used to prepare class **F** copolymer.*

Hydrosilylation of POSS **39** and spacer **67** (***Figure 5.10***) at room temperature with catalyst concentrations of 0.01, 0.05 and 0.10 mol% generated copolymers **F1**, **F2** and **F3** within 20 minutes of catalyst addition.

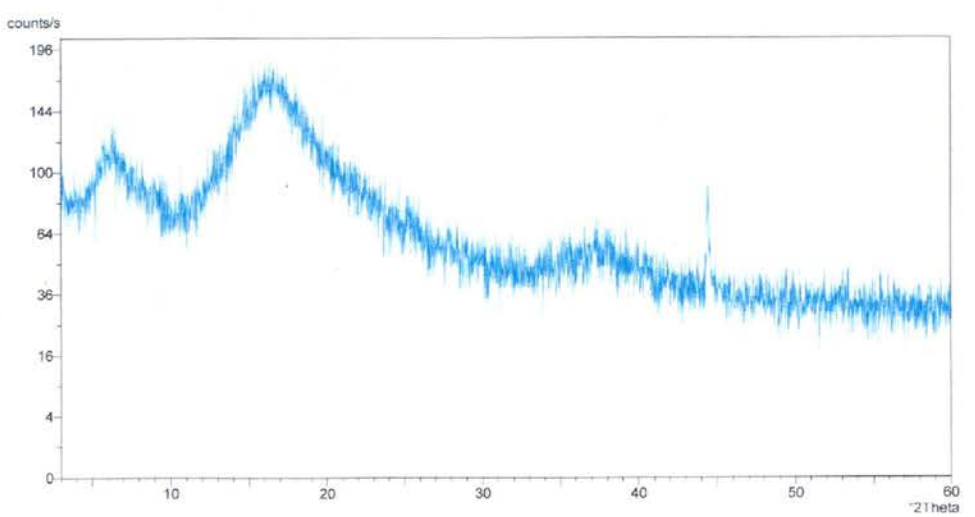


***Figure 5.11.** Powder pattern XRD for copolymer **F4**.*

Powder XRD again suggests an underlying structure (***Figure 5.11***) but again, the data obtained cannot be attributed to pores. Unlike the **D** and **E** class copolymers, the **F** class materials have a glassy appearance and do not have the same affinity for

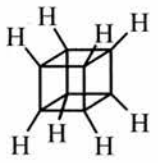
statically charged bodies. Despite these differences, the **F** class copolymers are also non-porous. Even when heated to 80 °C with 0.10 mol% catalyst, porous materials are not generated.

The NMR data, indicates a high yield from the hydrosilylation reaction, with only trace quantities of Si-H and vinyl groups being detected. Combined with the rapid gelation times observed for these copolymers, this suggests that the reaction between the precursors is facile and that the flexible nature of the functional groups attached to **39** facilitate the reaction. In addition, the length of the functional groups bound to the POSS and the linkages established between the POSS as the copolymer is forming (this includes the spacer unit and the functional groups of the POSS cubes) could allow easy structural interpenetration within the forming copolymer.

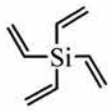
As the gelation in **F** class copolymers is very rapid when compared to that observed for **D1**, it may be concluded that spacer **67** is not solely responsible for the failure of the **D** class copolymerisations. It may be the case that **39** interacts positively with the catalyst, encouraging the reaction despite any inadequacies in the interaction between **67** and the catalyst.

The FTIR spectra for the **F** class copolymers do not contain any notable absorptions for vinyl or Si-H groups which tallies with the high degree of cross-linking observed in the NMR data. When compared with the spectra for **E** and **D** class copolymers, very similar absorptions can be noted, but the degree of absorption in the fingerprint region is much higher in the **F** class copolymers.

*Copolymers class **G**.*



2



68

***Figure 5.12.** Precursor **2** and **73** used to prepare class **G** copolymer.*

Despite the lack of success in the preparation of porous solids by copolymerising POSS cubes with spacers **66** and **67**, porous materials were prepared by hydrosilylating cube **2** with **68** (***Figure 5.12***). Using a catalyst concentration of 0.01 mol% at room temperature produced glassy non-porous copolymer **G1**, but with a catalyst concentration of 0.10 mol % at room temperature, a porous copolymer, **G2**, with a surface area of 348 m^2g^{-1} was prepared. This was the first time that a porous material had been prepared in this series of experiments with this catalyst concentration at room temperature and a repeat reaction was performed to confirm these results. Using 0.10 mol% catalyst at 80 °C resulted in the preparation of a highly porous material with a surface area of 707 m^2g^{-1}. Due to delays in obtaining the surface area measurement, full characterisation of these materials was not possible but it is obvious from these results that contrary to previous studies, the use of spacer molecules and POSS cubes can produce porous solids.

The PXRD data obtained from **G1** (non-porous) and **G3** (porous) shows a slight difference between the two materials (***Figure 5.13***). The powder pattern for **G3** shows a form with a d spacing of 2.37 Å but this is not apparent in the powder pattern

for **G1**. Although in the other copolymer classes, forms suggested by the XRD data cannot be ascribed to porosity, it may be the case that this particular d spacing is associated with pores within **G3**.

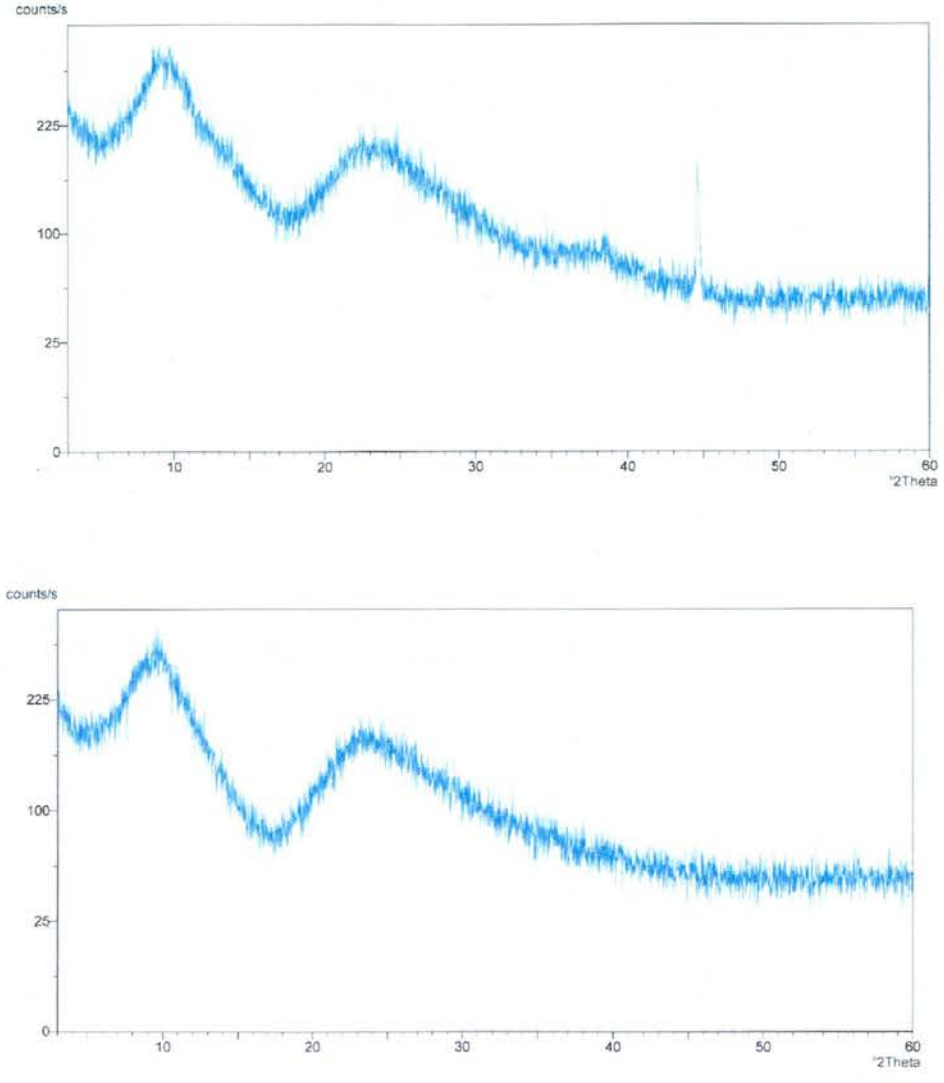


Figure 5.13. *Powder XRD patterns for porous* ***G3*** *(top) and non-porous* ***G1*** *(bottom)*

Precursors	Copolymer type	Catalyst (mol %)	Temp	Gel Time	Surface Area (m^2g^{-1})
2 + 7	**A1**	0.2 Chloroplatinic acid	110 °C	N/A	N/A
	A2	0.01 Pt (dvs)	RT	48 hours	<0.1
	A3	0.10 Pt (dvs)	RT	24 hours	<0.1
	A4	0.10 Pt (dvs)	80 °C	1hour	676
7 + 39	**B1**	0.01 Pt (dvs)	RT	24 hours	1.1
	B2	0.05 Pt (dvs)	RT	1 hour	0.57
	B3	0.10 Pt (dvs)	RT	1 hour	0.41
	B4	0.01 Pt (dvs)	80 °C	20 min	<1.5
	B5	0.05 Pt (dvs)	80 °C	20 min	374
	B6	0.10 Pt (dvs)	80 °C	20 min	569
	B7	0.20 Pt (dvs)	80 °C	15 min	575
	B8	0.50 Pt (dvs)	80 °C	10 min	523
39 + 65	**C1**	0.10 Pt (dvs)	RT	30 min	<0.1
2 + 67	**D1**	0.01 Pt (dvs)	RT	N/A	N/A
	D2	0.05 Pt (dvs)	RT	N/A	N/A
	D3	0.10 Pt (dvs)	RT	6 weeks	<0.1
	D4	0.10 Pt (dvs)	80 °C	N/A	N/A
7 + 66	**E1**	0.01 Pt (dvs)	RT	1 hour	<0.1
	E2	0.05 Pt (dvs)	RT	1 hour	0.16
	E3	0.10 Pt (dvs)	RT	1 hour	<0.1
	E4	0.10 Pt (dvs)	80 °C	20 min	<0.1
39 + 67	**F1**	0.01 Pt (dvs)	RT	3 hours, 40 min	<0.1
	F2	0.05 Pt (dvs)	RT	1 hour	<0.1
	F3	0.10 Pt (dvs)	RT	40 min	0.21
	F4	0.10 Pt (dvs)	80 °C	5 min	<0.1
2 + 68	**G1**	0.01 Pt (dvs)	RT	24 hours	<0.1
	G2	0.10 Pt (dvs)	RT	3 hours	340
	G3	0.10 Pt (dvs)	80 °C	20 min	707

Figure 5.14. *Table of reaction conditions, gellation times and surface areas for POSS based copolymers. Unless stated, platinum (dvs) was used as the catalyst.*

As can be seen in ***Figure 5.14***, the outcome of the copolymerisation reactions studied here is governed by the catalyst, reaction temperature and the type of precursors being combined.

Catalyst

Harrison and Kannengiesser used chloroplatinic acid to prepare a porous copolymer from POSS **2** and **7** but it was found that this catalyst did not generate copolymers under the conditions employed in this project. Although it was thought that the reaction conditions matched those employed by Harrison and Kannengiesser[2] this may not be the case as the published experimental detail was rather brief and may not have been comprehensive.

Once it had been established that chloroplatinic acid was not an effective catalyst in this particular situation, platinum (dvs) was used in its place. Copolymers could be readily prepared from POSS **2** and **7** with this catalyst and the subsequent experiments were all performed using it rather than chloroplatinic acid. It is recognised that in many cases platinum (dvs) is a more efficient catalyst than chloroplatinic acid and it is assumed that it is this greater efficiency which promotes reaction in this instance.[17]

Using platinum (dvs) at 0.01 and 0.05 mol% at room temperature successfully produced copolymers, but none are porous. This is contrary to the findings of Zhang *et al*[3] but, as has already been discussed, there may be slight differences between the methodology applied here and that previously reported. Using 0.10 mol% platinum

(dvs) at room temperature, copolymers of all classes were prepared and in the majority of cases, gelation was more rapid than that observed for lower catalyst concentrations. With the exception of **G2** however, none of these materials are porous.

Using 0.10 mol% platinum (dvs) at 80 °C, was found to consistently produce porous **A**, **B** and **G** class copolymers. The use of higher concentrations at 80 °C produced porous **B** class copolymers as expected, but the surface area of these materials did not exceed those previously obtained using 0.10 mol% catalyst at this temperature.

These observations suggest that the preparation of porous copolymers from two POSS precursors is at least partially dependent on the catalyst type and concentration employed. Low catalyst concentrations or catalysts of relatively low activity may form gels, but these do not generally produce high surface area solids at room temperature or at 80 °C. When a highly active catalyst is present at levels above what appears to be a threshold limit, consistent yields of porous copolymers can be prepared from POSS **2** paired with POSS **7** and POSS **39** paired with POSS **7** if the correct reaction temperature is used. When increased volumes of catalyst are present, an increase in surface area commensurate with the increase in catalyst volume is not observed.

Reaction temperature

Reactions at room temperature were found to routinely produce copolymers if an appropriate catalyst was employed and at a suitable concentration. Only copolymer **G2** was found to be porous however with copolymers from the other classes being non-porous. Increasing the reaction temperature to 80 °C during the preparation of **A**, **B** and **G** class materials using 0.10 mol% platinum (dvs) consistently produced copolymers with high surface areas. **G3** has a surface area more than double that of **G2** suggesting that the increase in temperature illicits an increase in porosity. It was observed that for the **A** and **B** classes the increase in reaction temperature did not simply increase the surface area of the copolymers prepared, but made the difference between porous and non-porous products. Preparing **B4** at 80 °C failed to produce porous materials indicating that an appropriate quantity of catalyst must also be present in the reaction mixture to allow the preparation of porous copolymers.

Precursors

By using a range of precursor molecules, it had been hoped that a range of porous materials could be prepared and correlation could then be drawn between their porosities and the types of precursor used. Only two new porous copolymer types and one which had previously been reported were prepared however, which prevents a detailed assessment being performed.

Copolymer **A4** was prepared from two POSS with relatively short functional groups (**2** and **7**) and no branches or aromatic components which could affect the copolymerisation process. This copolymer has a high surface area of 676 m^2g^{-1} which

is only to be expected due to the steric constraints of bringing two such precursors together.

Copolymer **B6** was prepared from POSS **7** and POSS **39** which results in the formation of longer inter-cube linkages than those found in **A4**. This copolymer has a lower surface area of 569 m^2g^{-1} which may reflect the greater degree of flexibility introduced by the longer functional groups of **39**, resulting in a denser material or even structural interpentration within the copolymer. The flexibility of these functional groups may be off-set by the presence of the dimethyl groups attached to them which could influence the formation of the copolymer through steric bulk. This steric bulk could act to "prop up" the copolymer structure as it forms, helping to maintain a high surface area.

Copolymer **C1** was prepared from two POSS with relatively long functional groups (**39** and **65**) incorporating two sets of dimethyl groups into the linkages between the POSS cores. Despite the presence of the dimethyl groups which would be expected to introduce a degree of porosity into this material through their steric bulk, this material was found to be non-porous. It may be the case that the extra freedom available to the functional groups of the precursors allows interpentration and compression of the structures through bending of the inter-cube links. Non-porous **A** and **B** class copolymers were also prepared before reaction conditions were identified that would prepare porous materials. It may therefore be the case that if appropriate reaction conditions could be found, they may illicit the formation of a porous **C** class copolymer. Studies of sol-gel systems suggest that such a porous copolymer should be possible but with a surface area smaller than that observed for **B6**.[18]

Surprisingly, the incorporation of aromatic silanes into the copolymers did not produce porous materials. No reaction occurred between POSS **2** and spacer **67** to form **D** class copolymers unless the reaction mixture was left for over 6 weeks and even then only a loose gel was formed. Rapid reaction occurred between POSS **39** and spacer **67** to form a series of **F** class copolymers which suggests that steric and/or electronic effects hamper reaction between **2** and **67**. POSS **39** has several atoms between the POSS core and the silicon hydride groups which would be expected to reduce or block any electronic effect. In addition, the length of the functional groups may allow better spacing of the reacting groups reducing any steric effect and improving the rate of reaction. Reactions between POSS **7** and spacer **66** were also rapid but also failed to produce porous materials.

Due to the steric restrictions associated with intra-POSS hydrosilylation of **7** and **66**, it is likely that this process will not occur and only inter-POSS reactions will proceed. As the product of the copolymerisation reaction is indeed a polymer, it may be assumed that this is the case. This implies that the POSS are linked through aromatic ring systems which have the potential to act as rigid units, resulting in a porous structure but only non-porous materials are observed. This suggests that some form of interpenetration is occurring during the formation of the copolymer producing a dense medium with a low surface area. This may also be the case for the **F** class copolymers although the longer functional groups of **39** may allow some intra-POSS reactions with **67**, but as a glassy material is formed, it may be assumed that most, if no all, of the hydrosilylations are due to inter-POSS reactions.

While the reactions involving the aromatic spacer units appear to agree with the findings of Hoebbel *et al*[1] and Agaskar,[10] copolymerising POSS **2** with tetravinylsilane (**68**) can produce a copolymer, **G3**, with a surface area higher than those obtained for **A** and **B** class copolymers. This suggests that linear spacer units do not lend themselves to the preparation of high surface area POSS but those that can form multi-dimensional links between POSS do. In effect, the tetravinylsilane may act as a functionally reduced POSS cube and produce copolymers that are similar to those produced by POSS-POSS copolymerisations. Due to delays in obtaining porosity measurements for the **G** class copolymers, samples of these copolymers were not available for NMR studies before the completion of this project and a detailed study of their properties was not possible.

Reaction mechanism

It was found that porous **A** and **B** class copolymers can be prepared using 0.10 mol% or higher platinum (dvs) catalyst and a reaction temperature of 80 °C. At room temperature, copolymers can be prepared using 0.01, 0.05 and 0.10 mol% platinum (dvs) but these are non-porous materials. Catalyst concentrations below 0.10 mol% with a reaction temperature of 80 °C do produce copolymers, but these are either non-porous or have a reduced porosity. These observations suggest that, for POSS-POSS systems, a rapid hydrosilylation is required to produce porous copolymers as this is supported by raised temperatures and higher catalyst concentrations.

It was observed that the POSS-POSS and POSS-tetravinylsilane copolymers were either porous with a high surface area or essentially non-porous. As catalyst

concentrations above 0.1 mol% do not produce surface areas noticeably above those obtained at 0.1 mol%, it would appear that the copolymerisation mechanism operates by two different routes leading to two different states. Rapid copolymerisation caused by high catalyst concentration and elevated temperatures locks the material in an open structure with a surface area governed by the geometric constraints of the POSS-POSS or POSS-tetravinylsilane mixture and, possibly, solvent molecules trapped within that structure. Slow copolymerisation may allow expulsion of solvent molecules from the forming network resulting in a denser material as well as interpenetration of molecular aggregations. This close interaction between the copolymer precursors could then allow more extensive cross linking than that observed in the porous materials. If the copolymerisation process does operate in this manner then it may be possible to prepare a porous copolymer from POSS **39** and **65** if the reaction is run at an elevated temperature.

As no porous copolymers were prepared from POSS-aryl precursor combinations, it may be assumed that these components react in a different manner to the POSS-POSS and POSS-tetravinylsilane systems. It is difficult to suggest a possible mechanism for these reactions. Performing the hydrosilylations at 80 °C with 0.10 mol% platinum (dvs) resulted in rapid gelation which suggests that for these precursors, rapid reactions do not produce porous materials. It is conceivable that the high mobility of the aryl spacers allows them to enter the pore spaces in the forming copolymer, resulting in interpenetration within the material.

Copolymer structures

Although PXRD suggests that these copolymers have some order to their structures, insufficient information can be gleaned from the data to provide detailed information on these materials. Direct comparison between porous and non-porous samples of **A** and **B** class copolymers show no discernible difference between materials from each class, although it is obvious that there is a difference.

As the XRD powder patterns obtained from the non-porous copolymers have similar features to those of the porous copolymers, features that are being observed are structures or forms within the copolymer as opposed to pore structures. The class **G** copolymers are an exception in this respect as a minor peak observed in the powder pattern from **G3** (porous) is absent from the powder pattern of **G1** (non-porous). This may simply be an artefact as time did not allow for additional samples of **G1** and **G3** to be analysed, but as this copolymer is very different from the others prepared, it may be real.

The surface area analysis of the porous copolymers indicates that there is a considerable range of pore sizes in all of the porous samples. This suggests a great deal of disorder in the structure of the copolymers, but in the case of **B6**, there is a higher concentration of pores in the 14 and 28Å regions while pores in samples of **A4** were confined to the micropore region. To confirm the observed results, repeat experiments were performed for each porous copolymer and these produced materials with consistent surface areas and independent preparation of **B6** by Clark Riddick also produced similar results.[16] The consistency which was observed across these

experiments suggests that the reaction mechanism does offer a degree of order and control.

Although the porous copolymers prepared are all robust glassy solids, there appears to be a degree of flexibility within their structures. Rigid porous solids normally exhibit a simple adsorption/desorption plot but the porous copolymers prepared in these experiments all exhibit hysteresis between the adsorption and desorption processes during the surface area measurements (***Figure 5.15***).

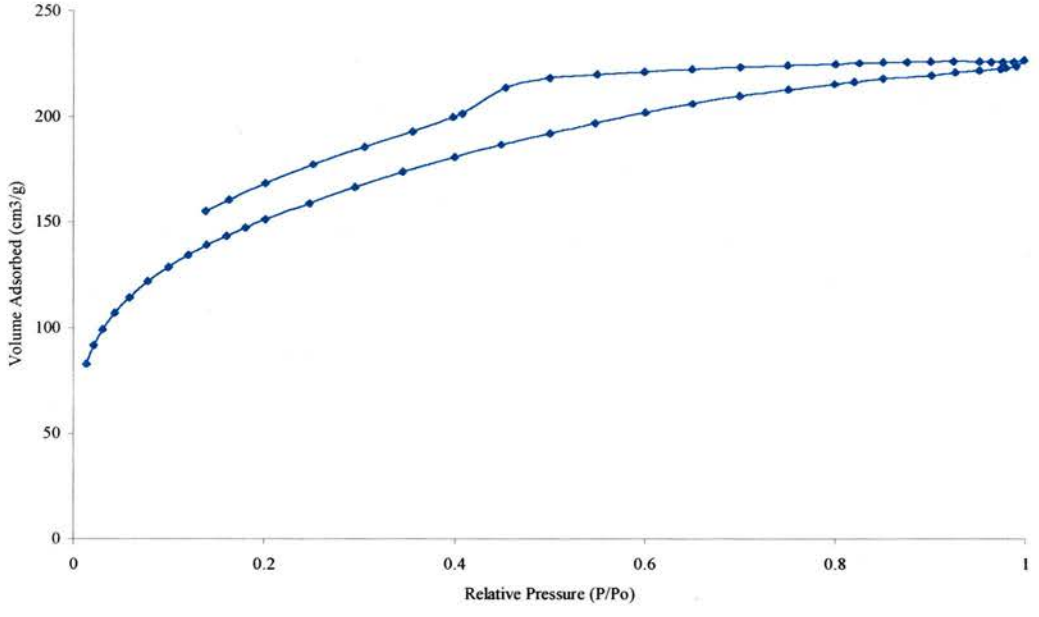


Figure 5.15 *. A typical adsorption/desorption isotherm plot for the porous copolymers prepared in this study. The example presented is for copolymer* ***B6****.*

This hysteresis indicates that that the desorption of the nitrogen is retarded relative to the uptake of nitrogen during the adsorption phase. This suggests that on entering the polymer structure the nitrogen causes the fabric of the copolymers to

swell, deforming the pores and closing off some of the narrower openings. During the desorption phase, the movement of the nitrogen from within the material is inhibited.

Although without undertaking further studies this theory cannot be confirmed, the functional groups used in these polymers are relatively flexible making this explanation for the observed isotherm viable. To confirm if this is in fact the case, a copolymer would have to be prepared with rigid groups which would produce a material that may flex to only a small extent.

Drying Effects

It should be noted that the manner in which the polymeric gels were dried will have an effect on their porosity.[18] As solvents are removed from such gels, shrinkage can occur, reducing the size of the pores within the final structure. The copolymers prepared here were dried at 80 °C at atmospheric pressure to remove the bulk of the solvent at a relatively slow rate with drying under reduced pressure then being used to remove the last traces of the solvent. However, even this gentle drying process is likely to have caused shrinkage in the materials and if a high level or shrinkage has been occurring, the copolymers which have been determined to be non-porous may have had a degree of porosity when in the gel form.

Techniques such as supercritical drying can be applied to this type of material and could offer a means to minimise shrinkage in the copolymers. It may therefore be advisable to perform comparative studies between the approach to drying employed in these experiments and supercritical drying to determine if gels viewed as being non-

porous can be dried to yield porous solids. It may also be possible to use supercritical drying on the gels which are already known to give porous solids to produce materials with even higher surface areas.

Conclusions

A range of new POSS copolymers have been prepared including both porous and non-porous examples. It is apparent that both the reaction conditions and the reactants govern whether this type of material is porous or non-porous.

Hydrosilylation of POSS **7** and POSS **39** with 0.10 mol% or greater platinum (dvs) at 80 °C produces a highly porous copolymer with a structure that is ideal for POSS cleavage experiments. Performing a similar reaction with POSS **39** and POSS **65** at room temperature failed to produce a porous solid. A higher reaction temperature may produce such a material, but insufficient **65** was produced to allow further experiments.

Hydrosilylation of POSS cubes and aryl spacer units in an attempt to produce high surface area materials failed to produce any despite the use of reaction conditions that were successful for POSS-only pairings and mixture of POSS and tetravinylsilane. Copolymers were prepared in these reactions, but it is unclear why none were porous or if it will be possible to modify the methodology used to produce porous materials. Previous studies have indicated that the use of spacer units does not result in the formation of porous copolymers, but the principle behind this approach appears sound. To further investigate the behaviour of aryl systems in POSS based

copolymers, attempts should be made to prepare functionalised POSS bearing appropriate aryl groups thereby dispensing with the need to use spacer units. This would allow experiments to be performed to determine if the failure to produce porous materials was due to use of spacer units rather than a combination of POSS.

Hydrosilylation of hydrido POSS **2** with tetravinylsilane produced a high surface area solid. Although the tetravinylsilane can be viewed as a spacer unit, it can react in three dimensions allowing it to behave more like a POSS molecule than the linear aryl spacer units **66** and **67**. The ability of tetravinylsilane to be used with POSS in the preparation of porous materials bodes well for the inclusion of substituted POSS such as mixed metal or corner capped species bearing catalytically active components as these may not have the octa-functionality of normal POSS.

Although these materials were prepared in a manner which did not promote ordering of the copolymer structure, powder X-ray diffraction of the samples indicates a degree of order in the materials. Reproducible results were obtained from these experiments indicating that there must be a level of order in the copolymerisation process. In addition, it should be noted that the **B** class copolymers had pore sizes grouped around the 14 and 28 Å width region suggesting a directing influence driving the forming structure towards pores of this size.

It appears that rapid copolymerisation is required to produce porous solids using POSS with slower reaction causing the formation of non-porous materials. This means that to prepare porous materials a highly active catalyst, elevated temperatures and a relatively high catalyst concentration are required. When these are employed,

high surface area solids can be routinely prepared from copolymer classes **A**, **B** and **G**. These conditions may also promote the formation of porous **C** class copolymers, but insufficient starting materials were available to perform additional studies on them.

The porous copolymers all contain a number of functional groups that did not react during the hydrosilylation reaction. These are most probably due to POSS being locked into positions where their functional groups cannot reach a suitable counterpart. This may prove to be useful in the preparation of catalytic materials from these copolymers as it may be possible to attach catalytic functionalities to them at these points.

As an initial study into the preparation of new POSS-based copolymers, this investigation has provided sufficient information to warrant additional studies. The copolymers investigated should be analysed in greater depth, in particular, efforts should be made to determine the origins of the features observed during the XRD studies. If an insight can be gained to the underlying structure of the copolymers prepared here, it may be possible to exert more control over their preparation.

Experimental

General. Vinylmagnesium bromide in hexanes (Aldrich), dimethylchlorosilane (Lancaster), chloroplatinic acid (Aldrich), platinum divinyltetramethyldisiloxane in siloxanes (Aldrich), tetravinylsilane (Aldrich), dibromobenzene (Aldrich), magnesium

turnings (Lancaster), vinyldimethylchlorosilane (Aldrich), iodine (Fisher), acetone (Fisher), ethanol (Fisher) and argon (BOC) were used as supplied. THF (Fisher) was distilled from sodium under nitrogen. Isopropanol (Fisher) was dried with calcium hydride (Aldrich) and distilled on to Linde type 4A molecular sieves (Prolabo). Information on the analytical equipment and techniques is provided in **Appendix B**.

Preparation of 0.20 M chloroplatinic acid solution. Prepared as in **Chapter 2** (page 75).

Preparation of 0.02 M chloroplatinic acid solution. Chloroplatinic acid (0.0820g, 0.2 mmol) was placed in a 10 cm^3 volumetric flask under a constant flow of argon. The solution was made up with dry isopropanol, capped with an argon blanket and refrigerated for storage.

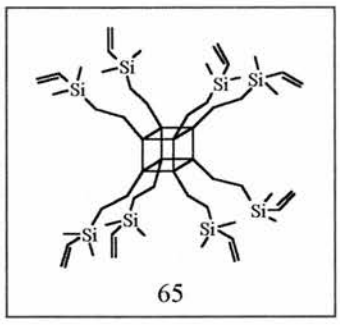
Preparation of 0.002 M platinum (dvs) solution. Platinum divinyltetramethyldisiloxane in siloxanes (0.096 cm^3, 1.04 M) was placed in a 50 cm^3 volumetric flask under a constant flow of argon. The solution was made up with dry toluene, capped with an argon blanket and refrigerated for storage.

Preparation of $[SiO_{3/2}H]_8$ (2). Prepared as in **Chapter 2** (page 74).

Preparation of $[SiO_{3/2}C_2H_3]_8$ (7). Prepared as in **Chapter 2** (page 94).

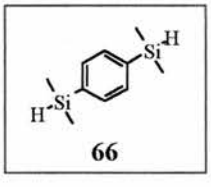
Preparation of $[SiO_{3/2}C_2H_4Si(CH_3)_2H]_8$ (39). Prepared as in **Chapter 3** (page 156).

Preparation of $[SiO_{3/2}C_2H_4Si(CH_3)_2C_2H_3]_8$ (65). THF (100 cm^3) and dimethylchlorosilane (1.404 g, 14.83 mmol) were added to dry **7** (1.001 g, 1.58 mmol) under an argon atmosphere. Choroplatinic acid solution (6 drops, 0.2M) was added and the solution was stirred overnight. The volatile components were removed by rotary evaporation and the off white solid obtained was re-dissolved in dry THF (100 cm^3) before vinylmagnesium bromide (5.5 cm^3, 2.5 M in hexanes) dissolved in dry THF (50 cm^3) was slowly added. The reaction mixture was stirred for 2 hours, added to aqueous sodium hydrogen carbonate solution (50 cm^3, 1.0 M) and then extracted with diethyl ether (3 × 50 cm^3). The combined extracts were dried over magnesium sulfate and passed through a silica gel column (220-240 mesh, diethyl ether elutant). Removal of the solvent produced a colourless solid which was recrystallised from acetone and ethanol to give needle like crystals (0.35 g, 17 % yield). Analysis confirmed the product as pure $[SiO_{3/2}C_2H_4Si(CH_3)_2C_2H_3]_8$.[14] ^1H NMR ($CDCl_3$) δ 6.01-5.65 (m, C**H**$_2$=C**H**-, 24H), 0.75 (s, -C**H**$_2$-, 16H), 0.62 (s, -C**H**$_2$-, 16H), 0.21 (s, Si-C**H**$_3$, 48H). ^{13}C NMR ($CDCl_3$) δ 138.23 (CH_2=CH-), 131.79 (CH_2=CH-), 6.24 (-**C**H_2-), 5.01 (-**C**H_2)-), -3.41 (Si-**C**H_3). Decomposition in air begins at 210 °C.



65

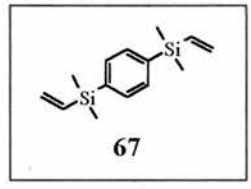
Preparation of $C_6H_4[Si(CH_3)_2H]_2$ (66). 1-,4-Dibromobenzne (5.876 g, 24.91 mmol) dissolved in THF (7 cm^3) was added to magnesium turnings (1.356 g, 55.78 mmol), dimethylchlorosilane (5.916 g, 62.52 mmol) and a single crystal of idoine dissolved in THF (30 cm^3) as per the method described by Liu *et al.*[15] Reaction began almost immediately and the resultant mixture was stirred for 2 hours before it was decanted into a solution of



66

aqueous sodium hydrogen carbonate (50 cm^3, 1M). The solution was extracted with diethyl ether (3 × 50 cm^3), washed with brine (50 cm^3) and dried over magnesium sulphate. After filtration, the solvent was removed by evaporation and the product purified by distillation (120 °C, 23 mmHg) to yield a clear oil which analysis confirmed as $C_6H_4[Si(CH_3)_2H]_2$ (**66**) (2.02 g, 42 %).[15] ^1H NMR ($CDCl_3$) δ 7.63 (s, C**H**, 4H), 4.50 (sept, J_{HH}=3.9 Hz, Si**H**, 2H), 0.43 (d, J_{HH}=4.1 Hz), Si-C**H**$_3$, 12H). ^{13}C NMR ($CDCl_3$) δ 138.58 (**C**H), 133.46 (**C**H), -3.78 (Si-**C**H_3).

Preparation of $C_6H_4[Si(CH_3)_2C_2H_3]_2$ (67). 1-,4-Dibromobenzne (5.903 g, 25.02 mmol) dissolved in THF (7 cm^3) was added to magnesium turnings (1.502 g, 61.79 mmol), dimethylvinylchlorosilane (7.545 g, 62.53 mmol) and a single crystal of idoine dissolved in THF (cm^3) using a method similar to that described my Liu *et al.*[15] A reaction began almost immediately and the resultant mixture was stirred for 2 hours before it was decanted into a solution of aqueous sodium hydrogen carbonate (50 cm^3, 1M). The solution was extracted with diethyl ether (3 × 50 cm^3), washed with brine (50 cm^3) and dried over magnesium sulphate. After filtration, the solvent was removed by evaporation and the product purified by distillation (160 °C, 24 mmHg) to yield a clear oil (3.33 g, 54 %). ^1H NMR ($CDCl_3$) δ 0.40 (s, Si-C**H**$_3$, 12H), 5.80-6.44 (m, C**H**=C**H**$_2$, 6H), 7.59 (s, C**H**, 4H). ^{13}C NMR ($CDCl_3$) δ 139.26 (**C**H), 137.91 (H_2C=CH-), 133.17 (**C**H), 132.89 (H_2C=CH-), -2.94 (Si-**C**H_3).



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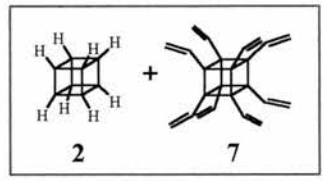
Copolymer class A.



Hydrosilylation at 110 °C using 0.20 mol % chloroplatinic acid (A1). Dry toluene (13.5 cm^3) was added to POSS **2** (0.201 g, 0.473 mmol) and POSS **7** (0.299 g, 0.472 mmol) under an argon atmosphere. The solution was degassed after cooling to approximately -78 °C and allowed to come to room temperature. Chloroplatinic acid in isopropanol (0.94 cm^3, 0.02M) was added to the silsesquioxane solution which was then refluxed for 18 hours. No perceptible change occurred within the solution which was then heated for a further 18 hours with no gelation occurring.

The solvent was evaporated from the reaction mixture and the resultant solid was analysed by NMR. ^{1}H NMR ($CDCl_3$) δ 6.14 - 5.82 (m, C**H**=C**H**$_2$, ~24H), 4.20 (s, **H**-SiO_3, ~8H), 0.59 (s, -C**H**$_2$-C**H**$_2$-, trace).

Room temperature hydrosilylation using 0.01 mol % Pt (dvs) (A2). Dry toluene (13.5 cm^3), POSS **2** (0.201 g, 0.473 mmol) and POSS **7** (0.299 g, 0.472 mmol) were prepared as in the previous experiment. Platinum (dvs) complex in toluene (0.19 cm^3, 2 mM) was added to the silsesquioxane solution which was then allowed to come to room temperature. No perceptible change occurred within the solution over 24 hours but a gel had formed within 48 hours. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried under reduced pressure (100 °C, 0.2 mmHg) to produce a glassy solid (0.40 g). Surface area (BET) : $<0.1 m^2 g^{-1}$. υ_{max}/cm^{-1} (KBr disk) 3029 (w), 2985 (w), 2964 (w), 2291 (w, Si-H), 1600

(vw, C=C), 1412 (w), 1264 (m), 1112 (vs, Si-O), 1000 (w, $CH=CH_2$), 964 (w, $CH=CH_2$), 850 (m, Si-H), 784 (m), 702 (m), 620 (m), 568 (m), 460 (m, Si-O).

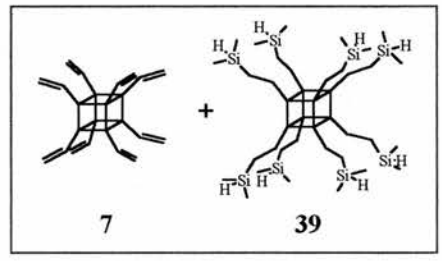
Room temperature hydrosilylation using 0.10 mol % Pt (dvs) (A3). Dry toluene (13.5 cm^3), POSS **2** (0.200 g, 0.471 mmol), POSS **7** (0.299 g, 0.472 mmol) and platinum (dvs) complex in toluene (1.88 cm^3, 2 mM) were prepared as for copolymer **A2**. A gel formed over a period of 24 hours and was allowed to stand for an additional 48 hours. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried under reduced pressure (100 °C, 0.2 mmHg) to produce a glassy solid (0.41 g). Surface area (BET) : <0.1 m^2g^{-1}. υ_{max}/cm^{-1} (KBr disk) 3022 (w), 2987 (w), 2964 (w), 2294 (vw, Si-H), 1604 (vw, C=C), 1409 (w), 1260 (vw), 1111 (s, Si-O), 964 (w, $CH=CH_2$), 853 (m), 780 (m), 705 (m), 624 (w), 569 (m), 462 (Si-O).

Hydrosilylation at 80 °C using 0.10 mol % Pt (dvs) (A4). Dry toluene (13.5 cm^3), POSS **2** (0.201 g, 0.473 mmol), POSS **7** (0.299 g, 0.472 mmol) and platinum (dvs) complex in toluene (1.89 cm^3, 2 mM) were prepared as in previous experiments. Once the catalyst had been added the solution was heated at 80 °C for 4 hours with a gel forming within the first hour. The reaction mixture was then allowed to stand for 12 hours at room temperature. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried in vaccuo (100 °C, 0.2 mmHg) to give a glassy solid (0.49 g). Surface area (BET): 676 m^2g^{-1}. Average pore radius: 11.31 Å. Average pore radius (BJH adsorption): 14.87 Å. Average pore radius (BJH desorption): 13.22 Å. υ_{max}/cm^{-1} (KBr disk) 3025 (w), 2985 (w), 2963 (w), 2295 (w,

Si-H), 1604 (w, C=C), 1410 (w), 1263 (vw), 1115 (s, Si-O), 1004 (m, $CH=CH_2$), 960 (w, $CH=CH_2$), 853 (m, SiH), 782 (m), 704 (m), 620 (w), 569 (m), 461 (Si-O).

Copolymer class B.

Room temperature hydrosilylation using 0.01 mol % Pt (dvs) (B1). Dry toluene (8.2 cm^3) was added to POSS **7** (0.160 g, 0.256 mmol) and POSS **39** (0.282 g, 0.256 mmol) under an argon



atmosphere. The solution was degassed after cooling to approximately -78 °C and then maintained at 0 °C using an ice bath. Platinum (dvs) complex in toluene (0.11 cm^3, 2 mM) was added to the silsesquioxane solution which was then allowed to come to room temperature. A gel was formed within 24 hours of catalyst addition and the mixture was left to stand for a further 12 hours at room temperature. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried in vaccuo (100 °C, 0.2 mmHg) to give a glassy solid (0.40 g). Surface area (BET): 1.1 m^2g^{-1}. υ_{max}/cm^{-1} (KBr disk) 3282 (w), 3070 (w, $C=CH_2$), 3026 (w, C=CH-), 2967 (w, CH_2/CH_3), 2927 (w, CH_2/CH_3), 2855 (w, CH_2/CH_3), 2579 (vw), 2365, 2345, 2271 (w), 2052 (vw, SiH), 1629 (m, C=C), 1421 (w, CH_2/CH_3), 1342 (w), 1277 (w), 1260 (w, $Si-CH_3$), 1111 (vs, Si-O), 1105 (vs, Si-O), 1089 (vs, Si-O), 1007 (s, $CH=CH_2$), 968 (m, $CH=CH_2$), 904 (m), 889 (m, $Si-CH_3$), 859 (w), 835 (w), 802 (w), 793 (w), 773 (w), 695 (w), 682 (w), 679 (w), 670 (m), 661 (w), 570 (s), 526 (w), 510 (w), 467 (s, SiO). Powder X-ray diffraction (Cu-Kα radiation 1.54056A) d spacings of major peaks : 10.99 Å, 5.84 Å, 4.12 Å, 2.39 Å.

Room temperature hydrosilylation using 0.05 mol % Pt (dvs) (B2). Dry toluene (8.2 cm^3), POSS **7** (0.181 g, 0.256 mmol), POSS **39** (0.319 g, 0.256 mmol) and platinum (dvs) complex in toluene (0.55 cm^3, 2 mM) were prepared as for **B1**. A gel was formed within 1 hour of catalyst addition and the mixture was allowed to stand for a further 12 hours at room temperature. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried in vaccuo (100 °C, 0.2 mmHg) to give a glassy solid (0.45 g). Surface area (BET): 0.57 m^2g^{-1}. υ_{max}/cm^{-1} (KBr disk) 3282 (w), 3071 (w, C=CH_2), 3024 (w, C=CH-), 2967 (w, CH_2/CH_3), 2926 (w, CH_2/CH_3), 2855 (w, CH_2/CH_3), 2579 (vw, CH_2/CH_3), 2271 (w), 2050 (w, SiH), 1629 (m, C=C), 1422 (w, CH_2/CH_3), 1342 (w), 1277 (w), 1260 (w, Si-CH_3), 1111 (vs, Si-O), 1106 (vs, Si-O), 1089 (vs, S-O), 1005 (s, CH=CH_2), 968 (m, CH=CH_2), 904 (m), 889 (m, Si-CH_3), 859 (w), 835 (w), 802 (w), 793 (w), 773 (w), 695 (w), 682 (w), 679 (w), 670 (m), 661 (w), 571 (s), 523 (w), 510 (w), 464 (s, Si-O).

Room temperature hydrosilylation using 0.10 mol % Pt (dvs) (B3). Dry toluene (8.2 cm^3), POSS **7** (0.181 g, 0.256 mmol), POSS **39** (0.319 g, 0.256 mmol) and platinum (dvs) complex in toluene (1.14 cm^3, 2 mM) were prepared as in previous experiments. A gel was formed within 1 hour of catalyst addition and the mixture was allowed to stand for a further 12 hours at room temperature. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried in vaccuo (100 °C, 0.2 mmHg) to give a glassy solid (0.42 g). Surface area (BET): 0.41 m^2g^{-1}. υ_{max}/cm^{-1} (KBr disk) 2950 (w, CH_2/CH_3), 2917 (w, CH_2/CH_3), 2891), 2850 (w, CH_2/CH_3), 2253 (w, SiH), 2103 (vw), 1715 (w), 1624 (m, C=C), 1447 (w), 1412 (m, CH_2/CH_3), 1255 (m, Si-CH_3), 1140 (vs, Si-O), 1105 (vs,

Si-O), 1088 (vs, Si-O), 1009 (s, $CH=CH_2$), 876 (m), 845 (m), 840 (m), 796 (m), 744 (w), 709 (w), 680 (m), 669 (m), 648 (w), 614 (w), 600 (w), 543 (m), 538 (m), 525 (m), 463 (s, Si-O). Powder X-ray diffraction (Cu-Kα radiation 1.54056A) d spacings of major peaks: 10.58 Å, 5.90 Å, 4.20 Å, 2.35 Å.

Hydrosilylation at 80 °C using 0.01 mol % Pt (dvs) (B4). Dry toluene (8.2 cm^3), POSS **7** (0.181 g, 0.286 mmol), POSS **39** (0.319 g, 0.286 mmol) and platinum (dvs) complex in toluene (0.11 cm^3, 2 mM) were prepared as in the previous experiments. Once the catalyst had been added the solution was heated at 80 °C for 4 hours with a gel forming within the first 20 minutes. The reaction mixture was then allowed to stand for 12 hours at room temperature. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried in vaccuo (100 °C, 0.2 mmHg) to give a glassy solid (0.48 g). Surface area (BET): <1.5 m^2g^{-1}. υ_{max}/cm^{-1} (KBr disk) 3282 (w), 3070 (w, $C=CH_2$), 3026 (w), 2967 (w, CH_2/CH_3), 2927 (w, CH_2/CH_3), 2855 (w, CH_2/CH_3), 2579 (vw, CH_2/CH_3), 2271 (w), 2052 (vw, SiH), 1629 (m, C=C), 1421 (w, CH_2/CH_3), 1342 (w), 1277 (w), 1260 (w, $Si-CH_3$), 1111 (vs, Si-O), 1105 (vs, Si-O), 1089 (vs, Si-O), 1007 (s, $CH=CH_2$), 968 (m, $CH=CH_2$), 904 (m), 889 (m, $Si-CH_3$), 859 (w), 835 (w), 802 (w), 793 (w), 773 (w), 695 (w), 682 (w), 679 (w), 670 (m), 661 (w), 570 (s), 526 (w), 510 (w), 467 (s, Si-O).

Hydrosilylation at 80 °C using 0.05 mol % Pt (dvs) (B5). Dry toluene (8.2 cm^3), POSS **7** (0.181 g, 0.286 mmol), POSS **39** (0.319 g, 0.286 mmol) and platinum (dvs) complex in toluene (0.11 cm^3, 2 mM) were prepared as in previous experiments. Once the catalyst had been added the solution was heated at 80 °C for 4 hours with a gel forming within the first 20 minutes. The reaction mixture was then allowed to stand

for 12 hours at room temperature. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried in vaccuo (100 °C, 0.2 mmHg) to give a glassy solid (0.50 g). Surface area (BET): 374 m^2g^{-1}. υ_{max}/cm^{-1} (KBr disk) 3034 (vw C=CH-), 2960 (w, CH_2/CH_3), 2923 (w, CH_2/CH_3), 2804 (vw), 2267 (vw), 2120 (w), 1634 (w, C=C), 1412 (w, CH_2/CH_3), 1278 (m), 1259 (m, Si-CH_3), 1145 (vs, Si-O), 1116 (vs, Si-O), 1007 (m, CH=CH_2), 967 (w, CH=CH_2), 888 (m, Si-CH_3), 843 (s), 808 (m), 760 (m), 722 (m), 474 (w), 461 (w, Si-O).

Hydrosilylation at 80 °C using 0.10 mol % Pt (dvs) (B6). Dry toluene (8.2 cm^3), POSS **7** (0.181 g, 0.286 mmol), POSS **39** (0.319 g, 0.286 mmol) and platinum (dvs) complex in toluene (1.14 cm^3, 2 mM) were prepared as in the previous experiments. Once the catalyst had been added the solution was heated at 80 °C for 4 hours with a gel forming within the first 20 minutes. The reaction mixture was then allowed to stand for 12 hours at room temperature. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried in vaccuo (100 °C, 0.2 mmHg) to give a glassy solid (0.48 g). NMR, Surface area (BET): 569 m^2g^{-1}. Average pore diameter (BJH adsorption): 32.8 Å. Average pore diameter (BJH desorption): 30.0 Å. Pore widths by DFT: 14 and 28 Å. υ_{max}/cm^{-1} (KBr disk) 3034 (vw C=CH-), 2960 (w, CH_2/CH_3), 2923 (w, CH_2/CH_3), 2804 (vw), 2267 (vw), 2120 (w), 1634 (w, C=C), 1412 (w, CH_2/CH_3), 1279 (m), 1259 (m, Si-CH_3), 1145 (vs, Si-O), 1112 (vs, Si-O), 1005 (m, CH=CH_2), 966 (w, CH=CH_2), 890 (m, Si-CH_3), 848 (s), 807 (m), 764 (m), 723 (m), 474 (w), 461 (w, Si-O). ^{13}C NMR δ 136.50 (minor peak, C=CH_2), 125.00 (minor peak, C=CH_2), 5.24 ($\underline{C}H_2$), 1.01 ($\underline{C}H_2$), -3.90 (Si-$\underline{C}H_3$), 29Si NMR δ 8.20 (minor peak), 5.17 (CH_2-$\underline{Si}(CH_3)_2$-CH_2), -10.80, -23.18 (minor peak, CH_2-$\underline{Si}(CH_3)_2$-H), -66.70 (CH_2-CH_2-$\underline{Si}O_3$), -81.15 (minor peak, CH_2=CH-$\underline{Si}$), -

141.90. Powder X-ray diffraction (Cu-Kα radiation 1.54056A) d spacings of major peaks: 11.06 Å, 5.85 Å, 4.17 Å, 2.40 Å.

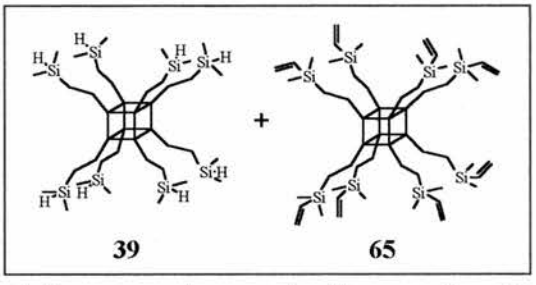
Hydrosilylation at 80 °C using 0.20 mol % Pt (dvs) (B7). Dry toluene (8.2 cm^3), POSS **7** (0.181 g, 0.286 mmol), POSS **39** (0.319 g, 0.286 mmol) and platinum (dvs) complex in toluene (0.11 cm^3, 2 mM) were prepared as in the previous experiments. Once the catalyst had been added the solution was heated at 80 °C for 4 hours with a gel forming within the first 15 minutes. The reaction mixture was then allowed to stand for 12 hours at room temperature. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried in vaccuo (100 °C, 0.2 mmHg) to give a glassy solid (0.48 g). Surface area (BET): 575 m^2g^{-1}. υ_{max}/cm^{-1} (KBr disk) 3850 (w), 3673 (w), 3459 (w), 2967 (w, CH_2/CH_3), 2923 (w, CH_2/CH_3), 2804 (vw), 2267 (vw), 2120 (w), 1632 (vw, C=C), 1412 (w, CH_2/CH_3), 1278 (m), 1259 (m, Si-CH_3), 1140 (vs, Si-O), 1109 (vs, Si-O), 1007 (m, CH=CH_2), 968 (vw, CH=CH_2), 888 (m, Si-CH_3), 843 (s), 807 (m), 760 (m), 721 (m), 474 (w), 464 (w, Si-O).

Hydrosilylation at 80 °C using 0.50 mol % Pt (dvs) (B8). Dry toluene (8.2 cm^3), POSS **7** (0.181 g, 0.286 mmol), POSS **39** (0.319 g, 0.286 mmol) and platinum (dvs) complex in toluene (5.72 cm^3, 2 mM) were prepared as in the previous experiments. Once the catalyst had been added the solution was heated at 80 °C for 4 hours with a gel forming within the first 10 minutes. The reaction mixture was then allowed to stand for 12 hours at room temperature. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried in vaccuo (100 °C, 0.2 mmHg) to give a glassy solid (0.49 g). Surface area (BET): 523 m^2g^{-1}. υ_{max}/cm^{-1}

(KBr disk) 3850 (w), 3673 (w), 3459 (w), 3034 (vw C=CH-), 2960 (w, CH_2/CH_3), 2923 (w, CH_2/CH_3), 2804 (vw), 2267 (vw), 2120 (w), 1637 (w, C=C), 1412 (w, CH_2/CH_3), 1278 (m), 1259 (m, Si-CH_3), 1143 (vs, Si-O), 1115 (vs, Si-O), 1004 (m, $CH=CH_2$), 967 (w, $CH=CH_2$), 885 (m, Si-CH_3), 842 (m), 808 (m), 760 (m), 720 (m), 471 (w), 461 (w, Si-O).

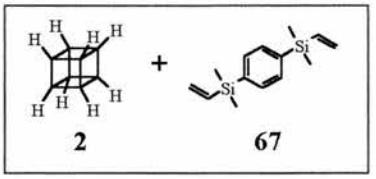
Copolymer class C.

Room temperature hydrosilylation using 0.10 mol % Pt (dvs) (C1). Dry toluene (5.8 cm^3) was added to POSS **39** (0.227 g, 0.204 mmol) and POSS **65** (0.270 g, 0.204 mmol) under an argon atmosphere. The solution was degassed after cooling to approximately -78 °C and then maintained at 0 °C using an ice bath. Platinum (dvs) complex in toluene (0.82 cm^3, 2 mM) was added to the silsesquioxane solution which was then allowed to come to room temperature. A gel was formed within 20 minutes of catalyst addition and was left to stand for 12 hours at room temperature. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried under reduced pressure (100 °C, 0.2 mmHg) to give a glassy solid (0.49 g). Surface area (BET): <0.1 m^2g^{-1}. υ_{max}/cm^{-1} (KBr disk) 2959 (m, CH_2/CH_3), 2903 (m, CH_2/CH_3), 2799 (w), 2356 (m), 2324 (m), 2103 (w, SiH), 1630 (w), 1411 (w, CH_2), 1256 (m, Si-CH_3), 1127 (s, Si-O), 1104 (s, Si-O), 1048 (m), 1012 (m, C=C), 949 (w, C=C), 890 (m, Si-CH_3), 834 (s), 806 (s), 760 (m), 704 (m), 653 (m), 627 (w), 562 (w), 530 (m), 467 (m, Si-O).



Copolymer class D.

Room temperature hydrosilylation using 0.05 mol % Pt (dvs) (D1). Dry toluene (10.2 cm^3) was added to POSS **2** (0.150 g, 0.355 mmol) and spacer **67** (0.349 g, 1.419 mmol) under an argon atmosphere. The solution was degassed after cooling to approximately -78 °C and then maintained at 0 °C using an ice bath. Platinum (dvs) complex in toluene (0.71 cm^3, 2 mM) was added to the silsesquioxane solution which was then allowed to come to room temperature. The solution was left stirring for 6 weeks but no gelation occurred.



2 **67**

Room temperature hydrosilylation using 0.05 mol % Pt (dvs) (D2). Dry toluene (10.2 cm^3), POSS **2** (0.151 g, 0.355 mmol), spacer **67** (0.349 g, 1.419 mmol) and platinum (dvs) complex in toluene (0.71 cm^3, 2 mM) were prepared as for **D1**. The solution was left stirring for 6 weeks but no gelation occurred.

The solvent was evaporated from the reaction mixture under reduced pressure and the resultant sludge was analysed by NMR. ^1H NMR ($CDCl_3$) δ 7.60 (s, C**H**, 32H),), 5.80-6.45 (m, C**H**=C**H**$_2$, 48H), 4.21 (s, **H**-SiO_3, 8H), 0.40 (s, Si-C**H**$_3$, 48H).

Room temperature hydrosilylation using 0.10 mol % Pt (dvs) (D3). Dry toluene (10.2 cm^3), POSS **2** (0.151 g, 0.355 mmol), spacer **67** (0.350 g, 1.420 mmol) and platinum (dvs) complex in toluene (1.42 cm^3, 2 mM) were prepared as in the previous experiments. After stirring for 6 weeks, a "loose" gel was formed as opposed to the firm gels obtained in the other copolymer classes. Drying produced a powdery solid

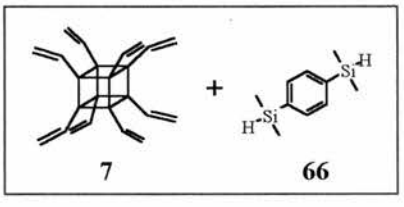
which was extremely difficult to manipulate due to a tendency to pick up static charge during handling (0.48g). Surface area (BET): <0.1 m^2g^{-1}. υ_{max}/cm^{-1} (KBr disk) 3421 (s), 3048 (w), 2995 (w), 2958 (m), 2900 (w), 2850 (w), 2804 (vw), 2260 (w, Si-H), 2117 (m), 1911 (vw), 1625 (m, aryl C), 1398 (w), 1380 (m), 1328 (w), 1257 (s, Si-CH_3), 1194 (m), 1138 (vs, Si-O), 1066 (vs), 1019 (s), 881 (m), 827 (s, aryl CH), 789 (s), 763 (m), 734 (w), 695 (w), 663 (w), 608 (w), 558 (w), 497 (m), 471 (s, Si-O).

Hydrosilylation at 80 °C using 0.10 mol % Pt (dvs) (D4). Dry toluene (10.2 cm^3), POSS **2** (0.151 g, 0.355 mmol), spacer **67** (0.350 g, 1.422 mmol) and platinum (dvs) complex in toluene (1.42 cm^3, 2 mM Once the catalyst had been added the solution was heated at 80 °C for 48 hours. No gelation was observed during this period.

The solvent was evaporated from the reaction mixture under reduced pressure and the resultant sludge was analysed by NMR. ^{1}H NMR ($CDCl_3$) δ 7.59 (s, C**H**, 32H),), 5.80-6.43 (m, C**H**=C**H**$_2$, 48H), 4.20 (s, **H**-SiO_3, 8H), 0.41 (s, Si-C**H**$_3$, 48H).

Copolymer class E.

Hydrosilylation using 0.01 mol % Pt (dvs) (E1). Dry toluene (10.3 cm^3) was added to POSS **7** (0.228 g, 0.36 mmol) and spacer **66** (0.280 g, 1.44 mmol) under an argon atmosphere. The solution was degassed after cooling to approximately -78 °C and then maintained at 0 °C using an ice bath. Platinum (dvs) complex in toluene (0.14 cm^3, 2 mM) was added to the silsesquioxane solution which was then



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allowed to come to room temperature. After 24 hours, no gel had formed and the solution was heated at 80 C for 7 hours with gel formation occurring within the first hour. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried in vaccuo (100 °C, 0.2 mmHg) to give small mica-like platelets (0.50 g). Surface area (BET): <0.1 m^2g^{-1}. υ_{max}/cm^{-1} (KBr disk) 3053 (w), 3000 (vw), 2955 (w, CH_2/CH_3), 2919 (w, CH_2/CH_3), 2900 (w), 2794 (vw), 2120 (w), 1917 (vw), 1629 (m), 1447 (m, aryl C), 1410 (w), 1382 (w), 1255 (m, Si-CH_3), 1116 (s, SiO), 884 (w), 838 (m), 810 (m, aryl CH), 756 (m), 687 (m), 669 (w), 651 (w), 598 (w), 548 (w), 497 (w), 459 (m, Si-O).

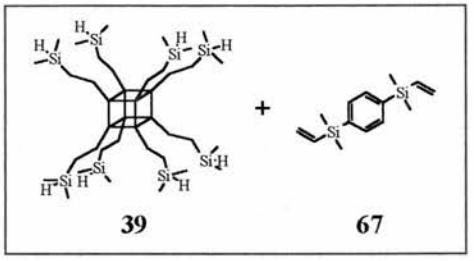
Room temperature hydrosilylation using 0.05 mol % Pt (dvs) (E2). Dry toluene (10.3 cm^3), POSS **7** (0.228 g, 0.36 mmol), spacer **66** (0.280 g, 1.44 mmol) and platinum (dvs) complex in toluene (0.72 cm^3, 2 mM) were prepared as for **E1**. A gel was formed approximately 1 hour after catalyst addition and the reaction mixture was left to stand for 12 hours at room temperature. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried in vaccuo (100 °C, 0.2 mmHg) to give small mica-like platelets (0.50 g). Surface area (BET): 0.16 m^2g^{-1}. υ_{max}/cm^{-1} (KBr disk) 3051 (w), 2999 (vw), 2960 (w, CH_2/CH_3), 2920 (w, CH_2/CH_3), 2900 (w, CH_2/CH_3), 2121 (w), 1632 (m), 1412 (w, Si-C), 1381 (w), 1252 (m, Si-CH_3), 1136 (s, Si-O), 1099 (s, Si-O), 1014 (m), 884 (w), 838 (m), 813 (m), 799 (m), 754 (m), 687 (m), 670 (m), 601 (m), 545 (m), 500 (m), 460 (m, Si-O).

Room temperature hydrosilylation using 0.10 mol % Pt (dvs) (E3). Dry toluene (10.3 cm^3), POSS **7** (0.228 g, 0.36 mmol), spacer **66** (0.280 g, 1.44 mmol) and

platinum (dvs) complex in toluene (1.44 cm^3, 2 mM) were prepared as in previous experiments. A gel was formed 1 hour after catalyst addition and the reaction mixture was left to stand for 12 hours at room temperature. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried in vaccuo (100 °C, 0.2 mmHg) to give small, mica-like platelets (0.50 g). Surface area (BET): <0.1 m^2g^{-1}. υ_{max}/cm^{-1} (KBr disk) 3051 (w), 2996 (vw), 2959 (w, CH_2/CH_3), 2922 (w, CH_2/CH_3), 2901 (w, CH_2/CH_3), 2804 (vw), 1921 (vw), 1821 (vw), 1634 (m), 1414 (w, Si-C), 1382 (w), 1262 (m, Si-CH_3), 1136 (s, Si-O), 1102 (s, Si-O), 1020 (m), 838 (m), 800 (m), 753 (m), 689 (m), 634 (w), 600 (w), 536 (m), 462 (m, Si-O).

Hydrosilylation at 80 °C using 0.10 mol % Pt (dvs) (E4). Dry toluene (10.3 cm^3), POSS **7** (0.224 g, 0.35 mmol), spacer **66** (0.276 g, 1.42 mmol) and platinum (dvs) complex in toluene (1.42 cm^3, 2 mM) were prepared as in the experiment which produced copolymer **F3**. Once the catalyst had been added the solution was heated at 80 °C for 4 hours with gelation occurring after approximately 20 minutes. The reaction mixture was then left to stand for a further 12 hours at room temperature. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried in vaccuo (100 °C, 0.2 mmHg) to give small, mica-like platelets (0.50 g). Surface area: <0.1 m^2g^{-1}. υ_{max}/cm^{-1} (KBr disk) 3051 (w), 2996 (vw), 2959 (w, CH_2/CH_3), 2922 (w, CH_2/CH_3), 2901 (w, CH_2/CH_3), 2804 (vw), 1921 (vw), 1821 (vw), 1634 (m), 1415 (w, Si-C), 1382 (w), 1262 (m, Si-CH_3), 1136 (s, Si-O), 1102 (s, Si-O), 1020 (m), 838 (m), 800 (m), 753 (m), 689 (m), 634 (w), 600 (w), 536 (m), 462 (m, Si-O).

Copolymer class F.



Room temperature hydrosilylation using 0.01 mol % Pt (dvs) (F1). Dry toluene (6.8 cm^3) was added to POSS **39** (0.265g, 0.238 mmol) and spacer **67** (0.234 g, 0.951 mmol) under an argon atmosphere. The solution was degassed after cooling to approximately -78 °C and then maintained at 0 °C using an ice bath. Platinum (dvs) complex in toluene (0.10 cm^3, 2 mM) was added to the silsesquioxane solution which was then allowed to come to room temperature. A gel was formed 3 hours, 40 minutes after catalyst addition and the reaction mixture was left to stand for 12 hours at room temperature. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried in vaccuo (100 °C, 0.2 mmHg) to give a glassy solid (0.49 g). Surface area (BET): <0.1 m^2g^{-1}. υ_{max}/cm^{-1} (KBr disk) 3044 (w), 2993 (w), 2950 (w, CH_2/CH_3), 2916 (w, CH_2/CH_3), 2784 (w), 2655 (vw), 2479 (vw), 2103 (vw, SiH), 1625 (m), 1406 (m, Si-C), 1378 (w), 1340 (vw), 1247 (m, Si-CH_3), 1133 (vs), 1101 (vs, Si-O), 1090 (vs), 1051 (s), 1018 (m), 876 (w, Si-CH_3), 832 (m), 808 (m), 804 (m), 795 (m), 766 (w), 727 (w), 713 (w), 680 (w), 670 (w), 620 (m), 607 (m), 561 (m), 538 (m), 528 (m), 499 (m), 469 (s, Si-O).

Room temperature hydrosilylation using 0.05 mol % Pt (dvs) (F2). The reaction employed to prepare the **F1** copolymer was repeated with dry toluene (6.8 cm^3), POSS **39** (0.265 g, 0.238 mmol), spacer **67** (0.234 g, 0.951 mmol) and platinum (dvs) complex in toluene (0.47 cm^3, 2 mM). A gel was formed 1 hour after catalyst addition and the reaction mixture was left to stand for 12 hours at room temperature. The

product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried in vaccuo (100 °C, 0.2 mmHg) to give a glassy solid (0.49 g). Surface area (BET): <0.1 m^2g^{-1}. υ_{max}/cm^{-1} (KBr disk) 3045 (w), 2981 (w), 2949 (w, CH_2/CH_3), 2912 (w, CH_2/CH_3), 2788 (w), 2662 (vw), 2469 (vw), 2101 (vw, SiH), 1625 (m), 1403 (m, Si-C), 1377 (w), 1246 (m, Si-CH_3), 1126 (vs, Si-O), 1097 (vs), 1092 (vs), 1049 (s), 1018 (m), 874 (w, Si-CH_3), 832 (m), 794 (m), 764 (w), 673 (w), 620 (m), 607 (m), 561 (m), 538 (m), 523 (m), 520 (m), 495 (m), 465 (s, Si-O).

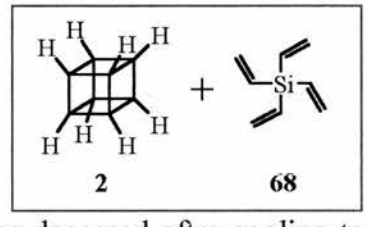
Room temperature hydrosilylation using 0.10 mol % Pt (dvs) (F3). The reaction employed to prepare the **F1** copolymer was repeated with dry toluene (6.8 cm^3), POSS **39** (0.265 g, 0.238 mmol), spacer **67** (0.234 g, 0.951 mmol) and platinum (dvs) complex in toluene (0.95 cm^3, 2 mM). A gel was formed 40 minutes after catalyst addition and the reaction mixture was left to stand for 12 hours at room temperature. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried in vaccuo (100 °C, 0.2 mmHg) to give a glassy solid (0.49 g). Surface area (BET): 0.21 m^2g^{-1}. υ_{max}/cm^{-1} (KBr disk) 3045 (w), 2991 (w, CH_2/CH_3), 2950 (w, CH_2/CH_3), 2912 (w, CH_2/CH_3), 2901), 2784 (w), 2654 (vw), 2472 (vw), 2104 (vw), 1623 (m), 1406 (m), 1377 (w), 1341 (vw), 1247 (m, Si-CH_3), 1131 (vs, Si-O), 1102 (vs, Si-O), 1090 (s, Si-O), 1049 (s), 1015 (m), 870 (w, Si-CH_3), 830 (m), 801 (m), 763 (w), 673 (w), 624 (m), 607 (m), 561 (m), 538 (m), 522 (m), 495 (m), 462 (s, Si-O).

Hydrosilylation at 80 °C using 0.10 mol % Pt (dvs) (F4). Dry toluene (6.8 cm^3), POSS **39** (0.264, 0.237 mmol), spacer **67** (0.234 g, 0.0.951 mmol) and platinum (dvs) complex in toluene (0.95 cm^3, 2 mM) were prepared as in the experiment which

produced copolymer **F3**. Once the catalyst had been added the solution was heated at 80 °C for 4 hours with gelation occurring within the first 5 minutes. The reaction mixture was then left to stand for 12 hours at room temperature. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried in vaccuo (100 °C, 0.2 mmHg) to give a glassy solid (0.49 g). Surface area (BET): <0.1 m^2g^{-1}. υ_{max}/cm^{-1} (KBr disk) 3045 (w), 2984 (w, CH_2/CH_3), 2949 (w, CH_2/CH_3), 2914 (w, CH_2/CH_3), 2787 (w), 2655 (vw), 2104 (vw, SiH), 1621 (m), 1411 (m, Si-C), 1377 (w), 1247 (m, Si-CH_3), 1126 (vs, Si-O), 1098 (vs, Si-O), 1090 (s, Si-O), 1050 (s), 1015 (m), 879 (w, Si-CH_3), 830 (m), 797 (m), 763 (w), 671 (w), 624 (m), 606 (m), 560 (m), 538 (m), 523 (m), 519 (m), 494 (m), 465 (s, Si-O).

Copolymer class G

Room temperature hydrosilylation using 0.01 mol % Pt (dvs) (G1). Dry toluene (20.5 cm^3) was added to POSS **2** (0.305 g, 0.717 mmol) and spacer **68** (0.195 g, 1.431 mmol) under an argon atmosphere. The solution was degassed after cooling to approximately -78 °C and then maintained at 0 °C using an ice bath. Platinum (dvs) complex in toluene (0.29 cm^3, 2 mM) was added to the silsesquioxane solution which was then allowed to come to room temperature. A gel was formed within 24 hours of catalyst addition and the reaction mixture was left to stand for a further 12 hours room temperature. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried in vaccuo (100 °C, 0.2 mmHg) to give a glassy solid (0.41 g). Surface area (BET): <5.3 m^2g^{-1}. υ_{max}/cm^{-1} (KBr disk)



3044 (w), 2964 (w, CH_2), 2901 (w, CH_2), 2877 (w, CH_2), 2351 (m), 2323 (m), 2261 (m), 1623 (w, C=C), 1458 (w), 1260 (s), 1149 (s, Si-O), 1091 (s), 1007 (m, $CH=CH_2$), 953 (m, $CH=CH_2$), 886 (m), 862 (w), 793 (m), 715 (m), 697 (m), 669 (m), 523 (w), 466 (m). Powder X-ray diffraction (Cu-Kα radiation 1.54056A) d spacings of major peaks: 9.37 Å, 3.87 Å.

Room temperature hydrosilylation using 0.10 mol % Pt (dvs) (G2). Dry toluene (20.5 cm^3), POSS **2** (0.305 g, 0.717 mmol), spacer **68** (0.195 g, 1.431 mmol) and platinum (dvs) complex in toluene (0.29 cm^3, 2 mM) were prepared as for **G1**. A gel was formed within 3 hours of catalyst addition and the reaction mixture was left to stand for a further 12 hours room temperature. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried in vaccuo (100 °C, 0.2 mmHg) to give a glassy solid (0.31 g). Surface area (BET): 340 m^2g^{-1}. υ_{max}/cm^{-1} (KBr disk) 3045 (w), 2964 (w, CH_2), 2903 (w, CH_2), 2878 (w, CH_2), 2356 (m), 2325 (m), 2257 (m, SiH), 1622 (w, C=C), 1458 (w), 1411 (w), 1262 (s), 1156 (s, Si-O), 1092 (s), 1009 (m, $CH=CH_2$), 951 (m, $CH=CH_2$), 885 (m), 863 (w), 796 (s), 715 (m), 697 (m), 669 (m), 521 (w), 468 (m, Si-O).

Hydrosilylation at 80 °C using 0.10 mol % Pt (dvs) (G3). Dry toluene (20.9 cm^3), POSS **2** (0.310, 0.730 mmol), spacer **68** (0.199 g, 1.460 mmol) and platinum (dvs) complex in toluene (2.92 cm^3, 2 mM) were prepared as in previous experiments. Once the catalyst had been added the solution was heated at 80 °C for 4 hours with gelation occurring within the first 20 minutes. The reaction mixture was then left to stand for 12 hours at room temperature. The product was recovered by filtration, dried for 48 hours at atmospheric pressure (80 °C) before being dried under reduced pressure (100

°C, 0.2 mmHg) to give a glassy solid (0.48 g). Surface area (BET): 723 m^2g^{-1}. Average pore radius (BET): 3.98 Å. υ_{max}/cm^{-1} (KBr disk) 3044 (w), 2961 (w, CH_2), 2903 (w, CH_2), 2875 (w, CH_2), 2355 (m), 2325 (m), 2257 (m, Si-H), 1622 (w), 1455 (w), 1411 (w), 1261 (s), 1147 (s, S-O), 1091 (m), 1008 (m, $CH=CH_2$), 951 (m), 886 (m), 863 (m, Si-H), 794 (s), 713 (m), 697 (m), 669 (m), 521 (w), 471 (m, Si-O). Powder X-ray diffraction (Cu-Kα radiation 1.54056A) d spacings of major peaks: 9.49 Å, 3.85 Å, 2.37 Å.

5.3 Reaction of Copolymerised POSS with Triflic Acid

Introduction

The degradation of POSS and silsesquioxanes by basic solutions is well known and they are regularly used to clean siloxane-contaminated glassware. Under controlled conditions however, alkalis can be used to selectively cleave one edge or corner of individual POSS cubes and allowing metal species or hetero atoms to be inserted into the molecules.[4, 5, 7] Strong acids can also be used to cleave POSS in this fashion although it has been proposed that the mechanism by which acid cleavage operates is slightly different to that assumed for base cleavage.

Both acid and base cleavage can be used to prepare novel POSS and offer a convenient route to preparing new POSS variants. Early studies investigated cleavage of POSS bearing cyclopentyl, cyclohexyl and cycloheptyl groups which undergo

facile reactions with acids and bases but are of limited synthetic utility. Feher and co-workers are currently attempting to produce more useful POSS by cleaving cubes such as the vinyl functionalised **7**, $[SiO_{3/2}C_2H_3]_8$, which could lead to the preparation of a range of synthetically useful molecules.[19] As has been demonstrated throughout this project, **7** is a synthetically useful POSS and the ability to insert transition metals into the structure of this molecule could lead to the preparation of new catalytically active materials.

During the experimental phase of this project, no reports of cleavage reactions being used with POSS copolymers were published and a preliminary study was undertaken to investigate the viability of this approach. Making use of the gram quantities of porous copolymer **B4**, it was hoped that triflic acid could be used to modify the material without destroying it and open up a new route to producing porous catalysts (***Figure 5.16***). By introducing catalytic species or supports for such species after preparation of an extended network or copolymer, the preparation of the material may be simplified. As time did not allow for an NMR study to be made on copolymers **G2** and **G3**, they were not included in the cleavage experiments as monitoring the effect of the acid would be difficult without NMR spectroscopy.

A range of products can be produced by POSS cleavage, both during the process itself and in post-cleavage rearrangements.[4, 19] It was anticipated that the presence of several products would make definitive characterisation difficult but that they would also make it obvious that cleavage had occurred within the material.

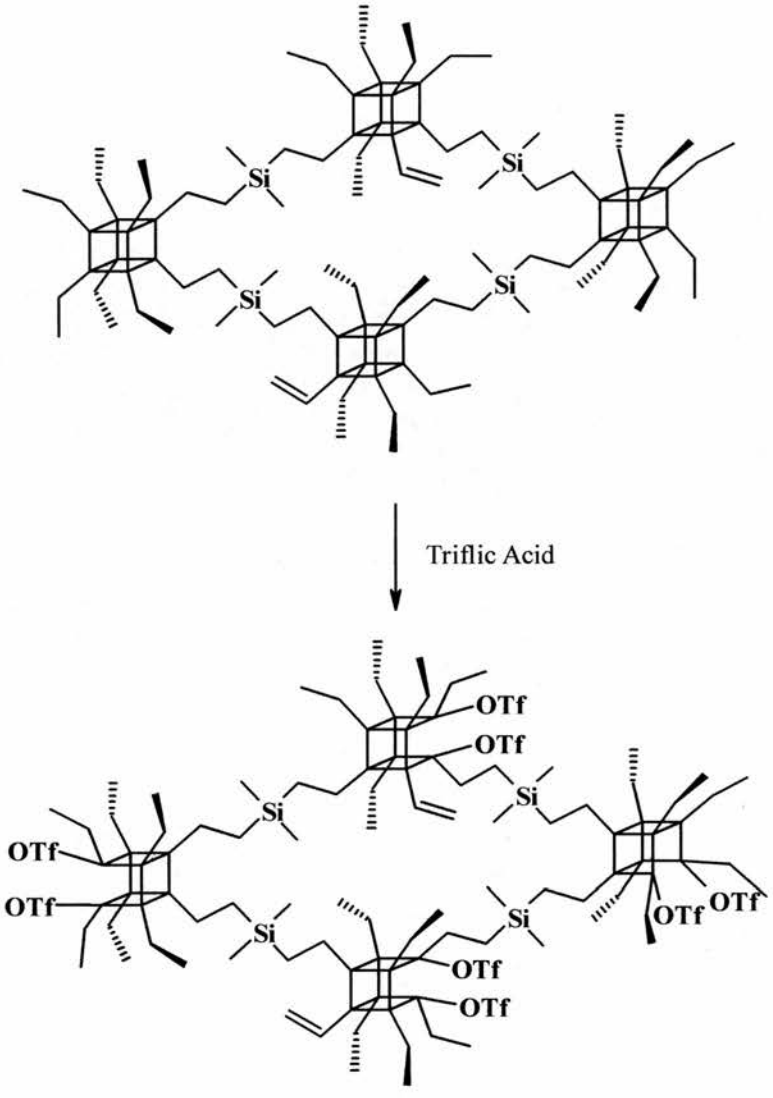


Figure 5.16. *Schematic of POSS copolymer cleavage using triflic acid.*

When discrete POSS undergo cleavage along a cube edge and are converted into di-silanols they can deform and flex in such a way as to avoid re-condensation of the cleaved edge. Under the sterically restricted conditions within a copolymer however, it was thought that hydroxyl groups would be likely to be brought back together and undergo re-condensation. To avoid this potential problem, triflic acid was selected to attempt cleavage in the copolymer as the products of reaction would

be triflate units rather than the silanol groups expected from a base promoted cleavage.

The principle problem associated with the proposed experiments was ensuring adequate reaction throughout the porous material, not just at its surface. For cleavage to occur throughout the copolymers, the acid has to penetrate the pores of the material but must also be removed when the reaction has progressed to the desired extent. Long reaction times could allow diffusion of the acid into the pore structure, but conversation with Prof. F. J. Feher indicated that over-reaction of discrete POSS was possible if they were left exposed to acid or base for too long.[6] This would mean that a large proportion if not all of the copolymer surface could be exposed to the acid but the surface material could be over-exposed. To encourage the acid to penetrate the copolymer, the reaction vessel was purged by alternately placing it under a slight vacuum and then re-pressurising it. It was hoped that this mechanism would remove gases from the voids within the material and force the acid solution into them.

The aim of these experiments was solely to identify whether acid cleavage and possibly base cleavage could be used to open cubes within a POSS copolymer without destroying the material. Any further work following on from positive results would be undertaken in subsequent research projects where a full investigation into the possibility of incorporating metal species into cubes cleaved by this process would be performed.

Results and Discussion

Due to the nature of the copolymer, solid state NMR and FTIR spectroscopy were the main analytical techniques used to determine if a reaction had taken place. The samples were studied using these techniques and BET surface area measurements before and after reaction with triflic acid. The measured surface area of the polymer does not change appreciably during the reaction suggesting that the triflic acid has not attacked the links between the cubes otherwise a change in surface area would be expected as pores were enlarged. Both the FTIR and NMR (***Figure 5.17***) spectra of the polymer change after exposure to triflic acid indicating that a reaction does take place.

Triflate groups have a characteristic band in IR spectra around the 1200 cm^{-1} region but this coincides with the characteristic Si-O-Si band making interpretation of the spectra difficult. Although definitive peak identification is not possible, there are changes in this region possibly indicating the introduction of triflate groups into the material. Additional peaks can be observed in the fingerprint region of the spectrum which are consistent with the addition of triflate groups but again, they are not solely indicative of these groups.

The NMR data indicates a definite change in the material, potentially due to changes in the POSS cube structure as elements of the spectra are no longer symmetrical. The resonance associated with the silicon atoms making up the corners of the POSS cube gains a shoulder which indicates a change in the conformation of a number of the cubes, possibly through cube cleavage. Resonances in the carbon and

proton spectra hint that triflate groups have been incorporated into the material but are far from conclusive.

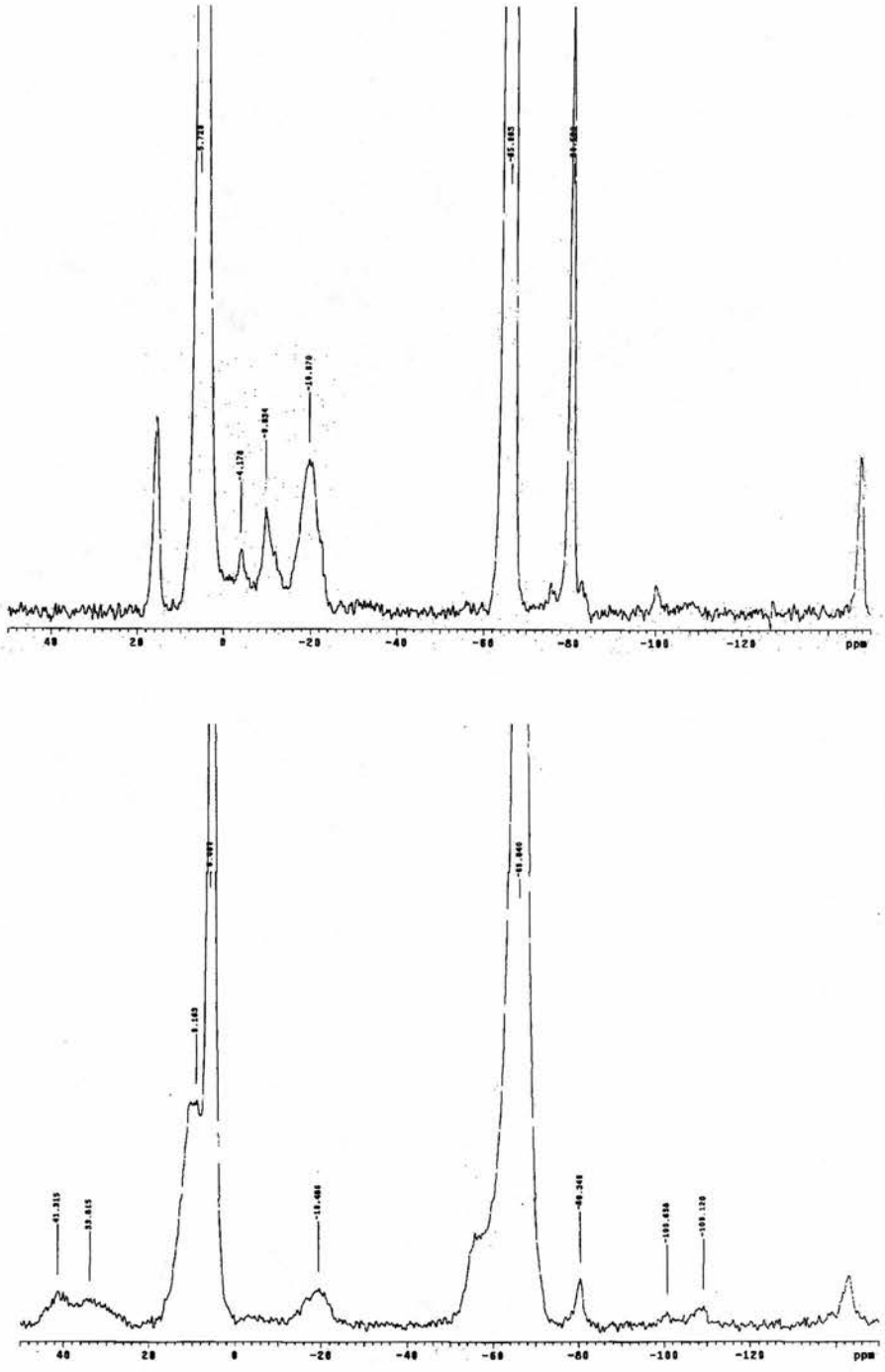


Figure 5.17. *^{29}Si NMR spectra for copolymer* ***B6*** *before reaction with triflic acid (upper spectrum) and after (lower spectrum)* ***B9****.*

From the experimental data, it is impossible to determine if the changes in the material are a surface effect or if the disruption of the original polymer extends into the material. On a practical level, reaction deep within the material would probably have a minimal effect on the outcome of reactions being catalysed by the material if it was being used in the powdered form. If the triflic acid could not penetrate the material then it would be unlikely that reactants in a catalysed reaction would do so. Further analysis of the polymer could possibly be undertaken by using a surface analysis technique such as DRIFTS to analyse a coarsely ground portion of the sample and then grind it further to expose material from deep within the granules. If the relative intensities of the product peaks are reduced after the grinding process, this would indicate that unreacted material from within the solid was being exposed.

Conclusions

From the data obtained, it is obvious that some form of reaction has taken place between the triflic acid and the copolymer. As there is no discernible change to the groups linking the cubes together, it may be assumed that the reaction that has taken place did not involve them directly. The NMR and FTIR data indicate greater disorder in the copolymer after interaction with triflic acid suggesting that cube cleavage has occurred, altering the structure of the silsesquioxane cores. Due to overlapping absorptions in the FTIR spectra and inconclusive NMR data, it cannot be determined if the disrupted copolymer has incorporated the triflic acid in the form of triflate groups or not. It is also unclear if further manipulation, such as the incorporation of hetero atoms or addition of catalyst support units, of the modified

copolymer is now possible. Time did not allow during this study, but ^{19}F NMR could provide additional information on the uptake of the triflic acid and the incorporation of triflate groups within the copolymer. It is therefore recommended that any subsequent studies where triflic acid is used as a cleaving agent should make use of this analytical technique.

As these experiments have suggested that it is indeed possible to cleave POSS cubes within copolymers, this process is now being studied by other research workers. Rather than using triflic acid, basic solutions are being used as they directly produce silanols during cube cleavage which is the ideal starting point for the incorporation of di- and tri-chloro titanium species. As it is difficult to determine the exact condition of the copolymer after cube cleavage experiments, the uptake of chloro-titanium species is being studied as an indication of the extent of cube cleavage.

Experimental

General. Triflic acid (Aldrich) and argon (BOC) were used as supplied. Acetonitrile (Ultrafine Ltd) was dried over Linde 4A molecular sieves (Prolabo) and distilled from calcium hydride (Aldrich) immediately before use. Information on the analytical equipment and techniques is provided in **Appendix B**.

Preparation of copolymer B6. B6 (1.002 g) was prepared as described in **Section 5.2**, page 245. υ_{max}/cm^{-1} (KBr disk) 3850 (w), 3673 (w), 3459 (w), 3034 (vw C=CH-), 2960 (w, CH_2/CH_3), 2923 (w, CH_2/CH_3), 2804 (vw), 2267 (vw), 2120 (w), 1634 (w, C=C), 1412 (w, CH_2/CH_3), 1278 (m), 1259 (m, Si-CH_3), 1145 (vs, Si-O), 1116 (vs,

Si-O), 1007 (m, $CH=CH_2$), 967 (w, $CH=CH_2$), 888 (m, $Si-CH_3$), 843 (s), 808 (m), 760 (m), 722 (m), 474 (w), 461 (w, Si-O). ^{13}C NMR δ 135.05 ($CH=CH_2$), 130.19 ($CH=CH_2$), 5.31 (-$\underline{C}H_2$-$\underline{C}H_2$-Si), -3.72 (Si-$\underline{C}H_3$). ^{29}Si NMR δ 5.72 (CH_2-$\underline{Si}(CH_3)_2$-CH_2), -9.83, -19.67 (CH_2-$\underline{Si}(CH_3)_2$-H), -65.96 (CH_2-CH_2-$\underline{Si}O_3$), -80.53 (CH_2=CH-$\underline{Si}O_3$). Surface area (BET): 569 m^2g^{-1}.

Cleavage of copolymer B6 (B9). Finely ground copolymer **B6** (0.502 g) was dried in vaccuo (100 °C, 0.2 mmHg, 2 hours) and brought back to atmospheric pressure under dry argon. Triflic acid (0.431 g, 2.87 mmol) was then added to a suspension of the copolymer in dry acetonitrile (10 cm^3) and the resulting mixture was cooled rapidly in an ice bath. The reaction vessel was placed under reduced pressure (26 mmHg) and returned to atmospheric pressure under argon 5 times before being removed from the cooling bath. After stirring for 1 hour at room temperature additional dry acetonitrile (20 cm^3) was added to the reaction mixture and half of the liquid was decanted with care being taken to avoid removing the modified copolymer. This operation was repeated three times before the remainder of the liquids were removed under vacuum (room temperature to 60 °C, 24 mmHg, 60 °C, 0.2 mmHg) to leave a pale tan solid (0.48 g). ν_{max}/cm^{-1} (KBr disk) 2960 (w, CH_2/CH_3), 2925 (w, CH_2/CH_3), 2801 (vw), 2366 (w), 2256 (w), 2115 (w) 1690 (w), 1415 (w, CH_2/CH_3), 1269 (m), 1260 (m), 1204 (m), 1146 (vs, Si-O), 1120 (s, Si-O), 1032 (m), 987 (m), 869 (m, $Si-CH_3$), 843 (m), 805(m), 761 (m), 724 (m), 708 (m), 648 (vw), 640 (w), 626 (w), 580 (w), 462 (w, Si-O). ^{13}C NMR δ 135.97, $CH=CH_2$), 129.02 ($CH=CH_2$), 122.00, 117.50, 28.92 (m), 21.63 (m), 5.56 (broad peak, -$\underline{C}H_2$-$\underline{C}H_2$-Si), -3.48 (Si-$\underline{C}H_3$). ^{29}Si NMR δ 41.32 (m), 33.82 (m), 9.16 (CH_2-$\underline{Si}(CH_3)_2$-CH_2, cleavage products), 6.08 (CH_2-$\underline{Si}(CH_3)_2$-CH_2), -

19.49 (CH_2-**Si**$(CH_3)_2$-H), -56.00 (broad, CH_2-CH_2-**Si**O_3, cleavage products), -65.84 (CH_2-CH_2-**Si**O_3), -80.35 (CH_2=CH-**Si**O_3). Surface area (BET): 523 m^2g^{-1}.

5.4 General Conclusions

The preparation of POSS/POSS and POSS/silane copolymers through hydrosilylation is a simple process but the combination of reaction conditions and starting materials govern whether these materials are porous or non-porous. Rapid gelation and short functional groups/spacer units appear to be the key to producing porous materials that have repeatable surface areas and internal structures. This observation and the PXRD data suggest that although the reactions which produce them have no obvious directing force, both the porous and non-porous copolymers have a degree of order in their structure.

On exposing porous copolymers to triflic acid, a reaction occurs which disrupts the structure of components within the material. Solid state ^{29}Si NMR indicates that this disruption is associated with the silicon atoms within the cubes themselves which suggests that cube cleavage is occurring within these materials. Confirmation of this cleavage reaction will be gained by hydrolysis of the trfilate groups and incorporation of dichloro-tripentadienyl-titanium into the structure and this work is currently being undertaken within our research group.

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Chapter 6 Conclusion

6.1 General Conclusions

Although well-ordered porous solids were not prepared, the other goals of this project have been achieved:

- Several new highly functionalised POSS have been prepared.
- Potential molecular building blocks have been synthesised.
- An investigation into the applicability of several synthetic techniques in the preparation of functionalised POSS has been performed.
- New POSS-based copolymers have been prepared.
- A porous copolymer appears to have been modified in such a way as to, allow it to be converted into a catalytic material.

Molecular Building Blocks

The preparation of molecular building blocks from POSS is not as easy as was first anticipated. Through a series of experiments however, a carboxylic acid-functionalised POSS (**18**) has been prepared which may lend itself to the preparation of network solids. Due to the time consuming task of developing this molecule, it was not possible to attempt the preparation of networks from it within the time scale of this project. Although it has not been prepared in a pure form and may in fact be unstable, the 3-isomer of this molecule (**19**) also appears to have been synthesised. In the course of preparing these molecules, two new dioxolane bearing POSS (**12** and

13) were prepared and from these two new aldehyde bearing POSS derivatives (**14** and **15**) were obtained.[1] Although the aldehyde-bearing POSS were not studied in any depth as part of this project, studies undertaken by other members of our research group have indicate that these molecules may make suitable precursors for catalyst supports.

Investigations into the preparation of pyridine-functionalised POSS resulted in the preparation of two new pyridine derivatives bearing vinylsilane groups, 3-(dimethyl-vinyl-silanyl)pyridine (**35**) and 4-(dimethyl-vinyl-silanyl-methyl)pyridine (**38**). Attempts were made to hydrosilylate these derivatives, 3-(dimethyl-silanyl)-pyridine and 4-vinylpyridine to suitably functionalised POSS. Although the results obtained are inconclusive, it appears that two new pyridine-bearing POSS (**44** and **45**) have been prepared through the reaction of POSS **39** with derivatives **35** and **38**. These materials must now be isolated and fully purified to allow confirmation of their preparation as time did not allow for this to be undertaken as part of this project.

Attempts to identify synthetic procedures applicable to POSS resulted in the preparation of a new thiophenol functionalised POSS (**52**) through a radical type reaction between thiophenol and vinyl functionalised POSS **7**. Although the reaction appears to go to completion, the product is unstable and reverts back to the starting materials over a period of time. Due to the instability of this type of molecule, only a preliminary study was made into the preparation of functionalised POSS from thiols.

Other reactions investigated included Heck-type arylation and the first step of the Gabriel synthesis. The Heck-type arylation experiments appear to have

successfully modified a vinyl functionalised cube (**7**), but in yields too low to be of use in the preparation of highly functionalised molecular building blocks. The first step of the Gabriel synthesis was used to convert a number of the iodomethyl groups of an iodomethylphenyl POSS (**50**) to phthalimide groups, but as for the Heck-type arylations, the yields obtained were too low to allow the preparation of highly functionalised molecular building blocks. Although both of these reactions currently appear to be of little use in the preparation of molecular building blocks, they may find applications elsewhere in, for example, the preparation of hard blocks for polymers.[2]

Copolymers

Although no extended networks were prepared during this project, several new POSS copolymer types have been prepared, two of which are porous. The two porous copolymers were prepared by combining POSS **7** with POSS **39** and POSS **2** with tetravinylsilane. Both of these materials have high surface areas of, typically, 569 and 707 m^2g^{-1} respectively. Although one of these porous copolymers was prepared using a "spacer" silane in conjunction with a POSS cube, attempts to prepare porous materials from POSS cubes and aryl spacer units produced only non-porous solids.

The preparation of porous copolymers was found to be affected by the type and concentration of the catalyst as well as the reaction temperature. Only hydrosilylation reactions above room temperature using catalyst concentrations of 0.10 mol% platinum (dvs) or higher routinely produced high surface area samples.

Although lacking a well ordered structure, powder XRD suggests the presence of a degree of order or an underlying structure in these materials but these results are inconclusive. This order was apparent in all of the copolymers, both porous and non-porous, suggesting that what was observed is not directly related pore structures within the materials.

Samples of porous copolymer were reacted with triflic acid in a manner similar to that used with discrete POSS.[3] Although the disordered nature of the copolymer hindered detailed analysis of the reaction products, NMR and FTIR spectroscopy data obtained from the samples reflect changes in the fabric of the copolymer. These changes appear to be centered on the POSS cube component of the material and suggest an increase in disorder. Although further work must be done to fully understand the outcome of these experiments and how the process may be developed further, it would appear that POSS within a porous network have been cleaved, possibly opening the door to a range of new porous catalysts.

6.2 Suggestions for Further Work

Molecular Building Blocks

The Heck arylation reactions performed as part of this project made use of a POSS with vinyl groups bound directly to the POSS core and gave a very low yield. This yield is probably due to the effect of the POSS core on the vinyl groups and higher yields may be obtained if this effect was removed or blocked. Additional

experiments should therefore be undertaken to determine if vinyl groups indirectly attached to POSS cores *via*, for example, ethyl linkages will produce higher yields. This would have been attempted as part of this project if it were not for the problematic preparation of POSS **65** which appears ideally suited to this type of experiment but was only prepared in sufficient quantities for the copolymerisation experiments (**Chapter 5**).

Further studies should be made into the preparation of pyridine-functionalised POSS through hydrosilylation. The experiments performed as part of this study produced interesting results and may have produced two of these POSS, but time did not allow for full purification and characterisation of these products. A detailed study, possibly employing alternative catalysts such as rhodium-based systems should now be undertaken to progress this work. The possibility of preparing pyridine-functionalised POSS through hydrolytic condensation should also be investigated as the techniques employed in this study successfully produced new pyridine-bearing silanes and may be capable of preparing trialkoxy silanes. Due to the basic nature of pyridine groups, it is suggested that efforts should be directed to the preparation alkoxysilanes rather than chlorosilanes and that base catalysis be employed in any hydrolytic condensations.

Although they were recognised as ideal groups for self-assembly processes,[4, 5] isonitrile-bearing POSS were not investigated in this project. Due to their potential suitability for self assembly, the preparation of such POSS should be investigated.

Extended Networks

Now that carboxylic acid-functionalised POSS have been prepared, efforts should be made to prepare extended networks from them. POSS **14** was found to be only sparingly soluble in methanol and insoluble in organic solvents, properties which may mean that well ordered hydrogen-bonded networks can be prepared from it under solvothermal or hydrothermal conditions.[6] Zinc (II) coordination has been demonstrated as being an effective means to produce extended structures by Yaghi *et al* and the techniques applied by that group will probably find application here.[7]

Copolymers

An investigation into the preparation of catalytic materials from acid- and base-cleaved copolymers should be made, but as was discussed in **Chapter 5**, this has already begun and will not therefore be discussed here.

Further studies should be made on the preparation of copolymer class **C** to determine if this copolymer type can be prepared in a porous form as is suggested by Loy and Shea.[8] Successful preparation of a porous copolymer of this type would indicate that porous materials can be prepared from POSS with lengthy functional groups. This would mean that incorporation of units such as ring systems and multiple bonds in the functional groups of POSS for self assembly would not be essential, simplifying the preparation of such molecules. In addition, the surface area of a porous **C** class copolymer may indicate a graduation in the properties of copolymer classes **A**, **B** and **C** correlating to the length of the functional groups of the precursors.

If this were the case, then it would provide confirmation that the properties of porous solids can indeed be controlled, at least to a certain extent, through the form of their precursors.

Attempts should be made to prepare copolymers using suitably functionalised mixed-metal POSS if these can be prepared.[9] The copolymerisation of POSS **2** and tetravinylsilane indicates that high surface area solids can be prepared through the reaction of octa-functionalised POSS and a tetra-functionalised unit. This suggests that it may therefore be possible to combine octa-functional POSS with metallated POSS which do not have the full complement of functional groups active towards hydrosilylation due to incorporation of a metal species.

The experiments into the preparation of copolymers from POSS cubes and aryl spacer units should be revisited in an effort to develop porous materials rather than the non-porous solids produced here. As well as the use of spacer units, the possibility of hydrosilylating POSS bearing aryl groups with a second POSS species should be investigated. This would indicate whether the non-porous materials produced in this project are due to the use of spacer units or the aromatic systems themselves.

If a route to producing porous copolymers using aryl spacer units such as those employed in this project can be developed, it may also be possible to use spacers derived from brominated thiophenes in the same manner as those derived from dibromobenzene.[10] This could result in the preparation of novel copolymers with novel properties associated with the thiophene groups.

6.3 Bibliography

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3. F. J. Feher, D. Soulivong, A. G. Eklund, *Chem. Commun.*, 1998, 399.
4. L. F. Mao, A. Mayr, *Inorg. Chem.*, 1996, **35**, 3183.
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7. O. M. Yaghi, C. E. Davis, G. Li, H. Li, *J. Am. Chem. Soc.*, 1997, **119**, 2861.
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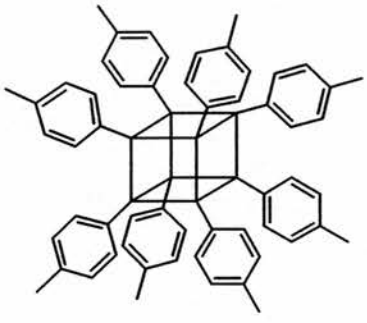
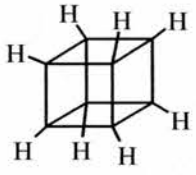
10. J. Ohshita, D. Kanaya, M. Ishikawa, *J. Organomet. Chem.*, 1994, **468**, 55.

Appendix A

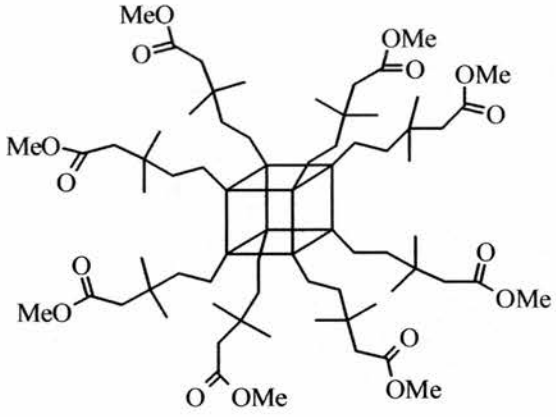
Molecular Structures



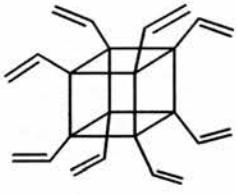
$[SiO_{3/2}C_7H_7]_8$ (**1**)



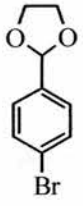
$[SiO_{3/2}H]_8$ (**2**)



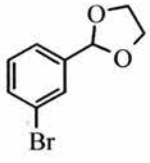
$[SiO_{3/2}CH_2CH_2C(CH_3)_2CH_2CO_2CH_3]_8$ (**3**)



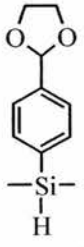
$[SiO_{3/2}C_2H_3]_8$ (**7**)



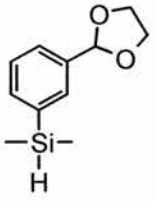
$BrC_6H_4CO_2C_2$ (**8**)



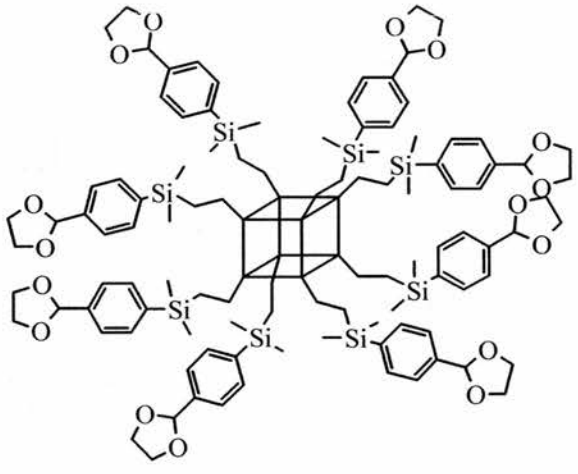
$BrC_6H_4CO_2C_2$ (**9**)



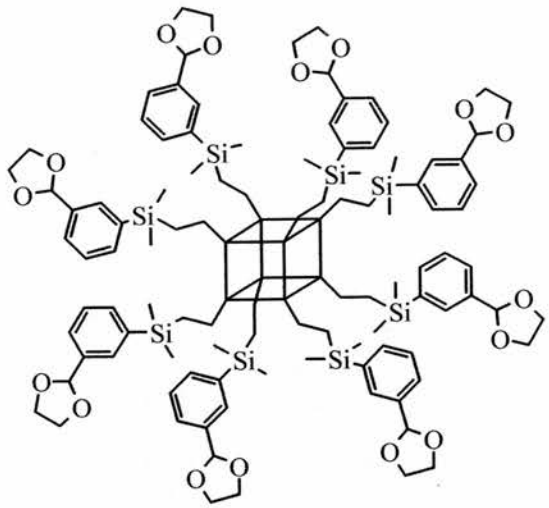
$HSi(CH_3)_2C_6H_4CO_2C_2$ (**10**)



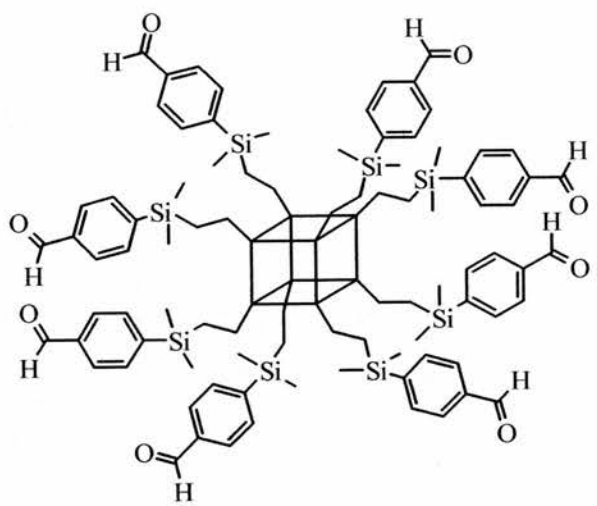
$HSi(CH_3)_2C_6H_4CO_2C_2$ (**11**)



$[SiO_{3/2}CH_2CH_2Si(CH_3)_2C_6H_4CHO_2C_2H_4]_8$ (**12**)



$[SiO_{3/2}CH_2CH_2Si(CH_3)_2C_6H_4CHO_2C_2H_4]_8$ (**13**)



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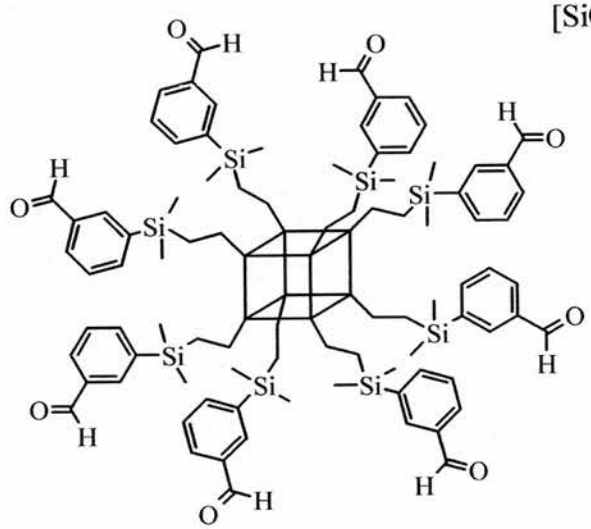
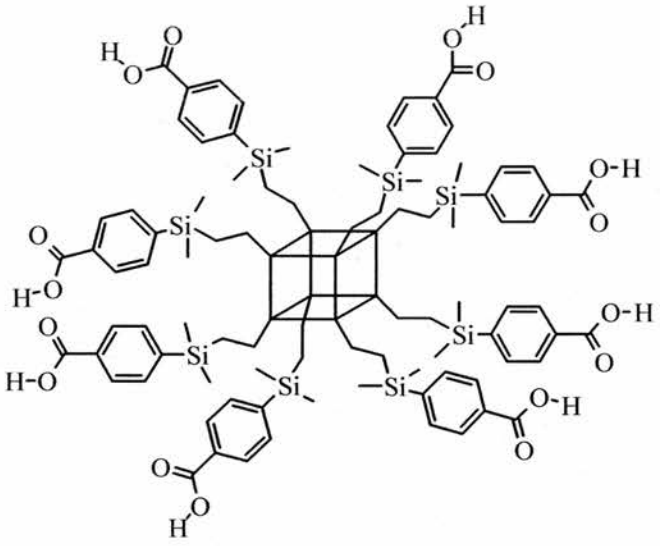
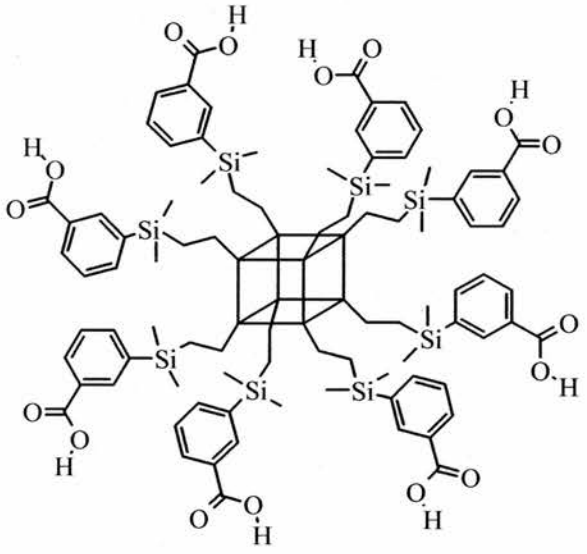


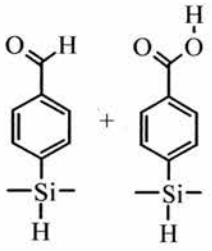
$[SiO_{3/2}CH_2CH_2Si(CH_3)_2C_6H_4CHO]_8$ (**15**)



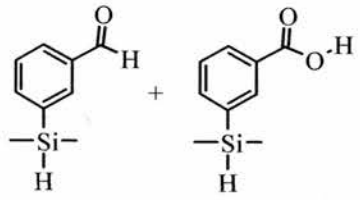
$[SiO_{3/2}CH_2CH_2Si(CH_3)_2C_6H_4COOH]_8$ (**18**)



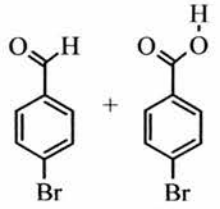
$[SiO_{3/2}CH_2CH_2Si(CH_3)_2C_6H_4COOH]_8$ (**19**)



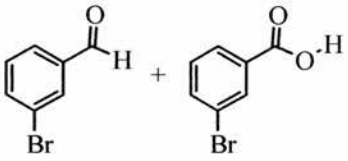
$HSi(CH_3)_2C_6H_4CHO$ and
$HSi(CH_3)_2C_6H_4COOH$ (**20**)



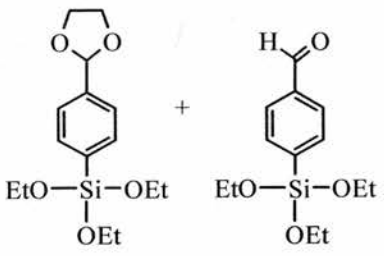
$HSi(CH_3)_2C_6H_4CHO$ and
$HSi(CH_3)_2C_6H_4COOH$ (**21**)



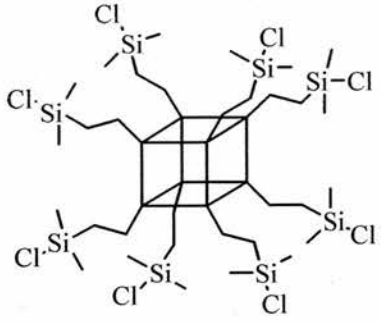
BrC_6H_4CHO and
BrC_6H_4COOH (**22**)



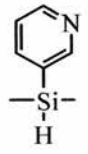
BrC_6H_4CHO and
BrC_6H_4COOH (**23**)



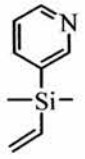
$(CH_3CH_2O)_3SiC_6H_4CHO_2C_2H_4$ and $(CH_3CH_2O)_3SiC_6H_4CHO$ (**27**)



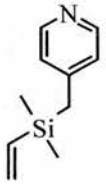
$[SiO_{3/2}CH_2CH_2Si(CH_3)_2Cl]_8$ (**28**)



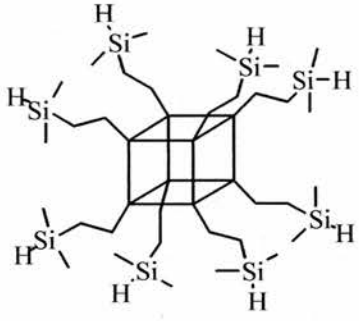
$HSi(CH_3)_2C_5H_4N$ (**34**)



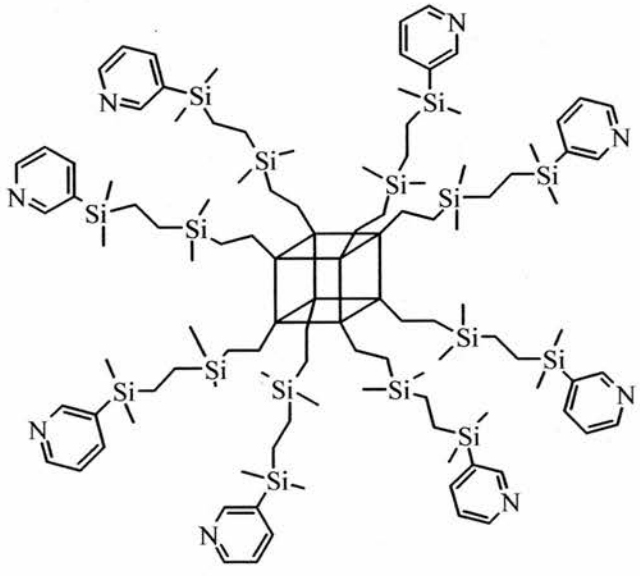
$CH_2CHSi(CH_3)_2C_5H_4N$ (**35**)



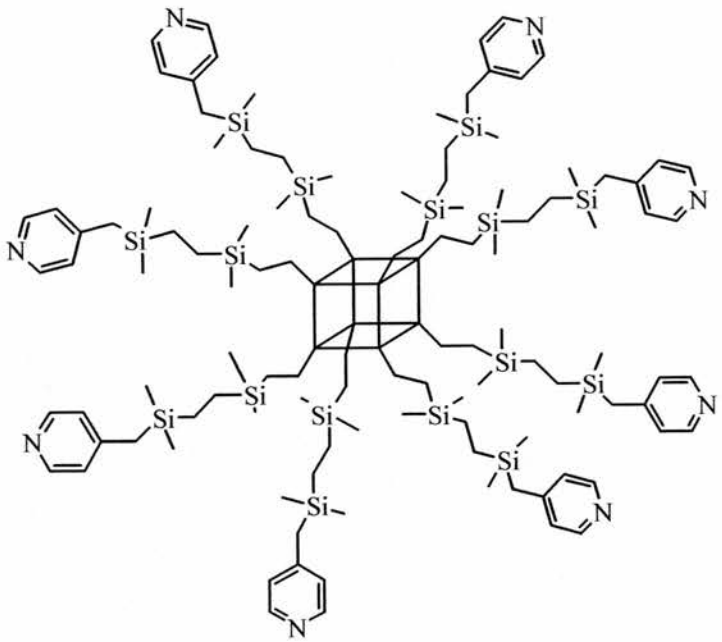
$CH_2CHSi(CH_3)_2CH_2C_5H_4N$ (**38**)



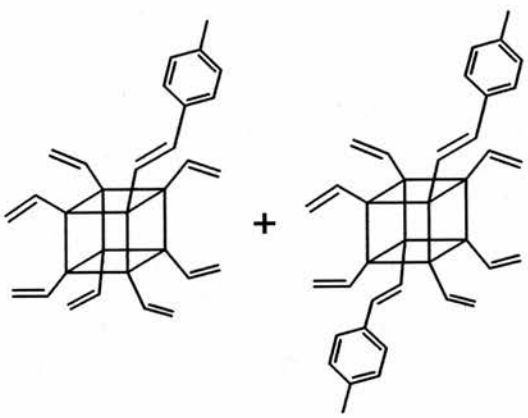
$[SiO_{3/2}CH_2CH_2Si(CH_3)_2H]_8$ (**39**)



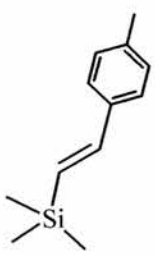
$[SiO_{3/2}C_2H_4Si(CH_3)_2C_2H_4Si(CH_3)_2C_5H_4N]_8$ (**44**)



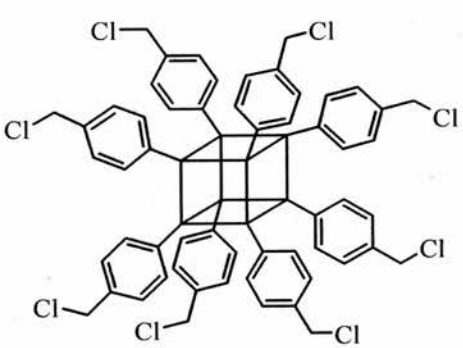
$[SiO_{3/2}C_2H_4Si(CH_3)_2C_2H_4\ Si(CH_3)_2CH_2C_5H_4N]_8$ (**45**)



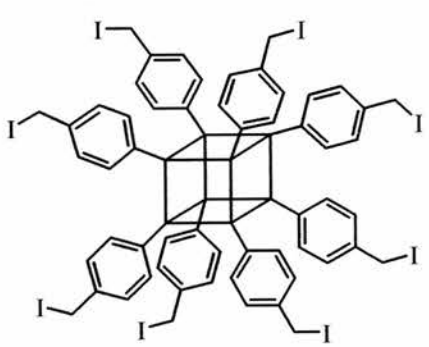
$(SiO_{3/2})_8(C_2H_3)_7(C_2H_2C_6H_4CH_3)$ and
$(SiO_{3/2})_8(C_2H_3)_6(C_2H_2C_6H_4CH_3)_2$ (**46**)



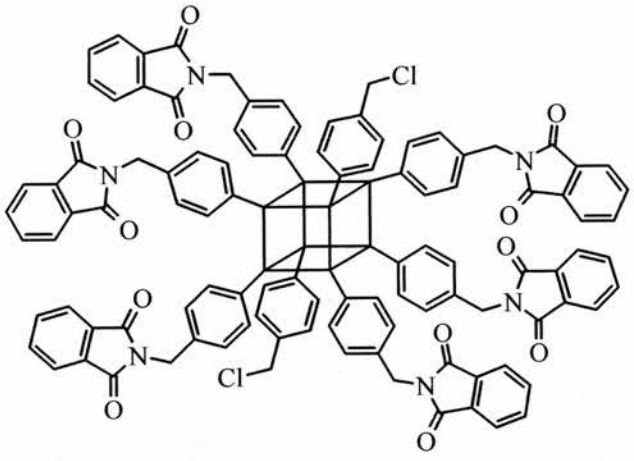
$[SiO_{3/2}C_6H_4CH_2Cl]_8$ (**48**)



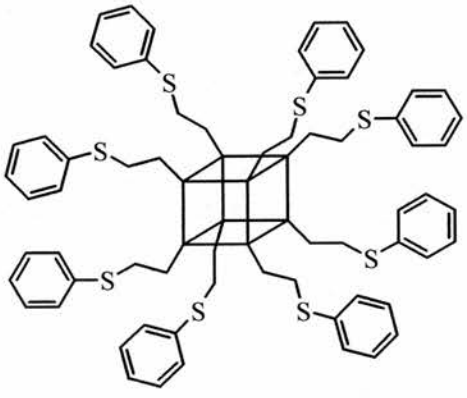
$[SiO_{3/2}C_6H_4CH_2Cl]_8$ (**49**)



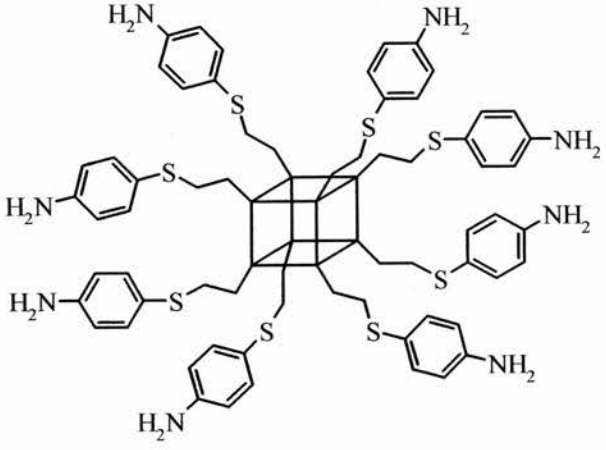
$[SiO_{3/2}C_6H_4CH_2I]_8$ (**50**)



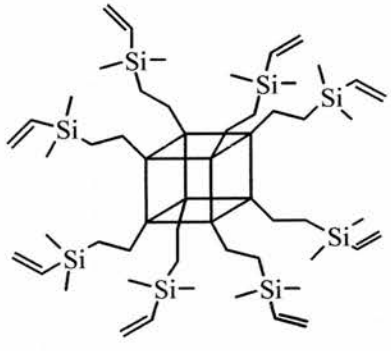
$[SiO_{3/2}]_8(C_6H_4CH_2Cl)(C_6H_4CH_2NC_2O_2C_6H_4)_7$ (**51**)
NB. Possible form.



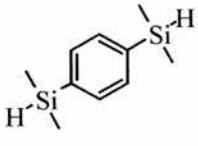
$[SiO_{3/2}C_2H_4\,SC_6H_5]_8$ (**52**)



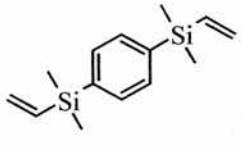
$[SiO_{3/2}C_2H_4\,SC_6H_5NH_2]_8$ (**61**)



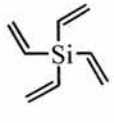
$[SiO_{3/2}C_2H_4Si(CH_3)_2C_2H_3]_8$ (**65**)



$[HSi(CH_3)_2]_2C_6H_4$ (**66**)



$[CH_2CHSi(CH_3)_2]_2C_6H_4$ (**67**)



$Si(CHCH_2)_4$ (**68**)

Appendix B

Instrumental Analysis

Solution NMR

^{1}H NMR spectra were recorded at 300 MHz, ^{13}C NMR spectra at 75.5 MHz on a Bruker AM300 spectrometer operating in Fourier transform mode with, for ^{13}C spectra, noise proton de-coupling. The NMR solvents were supplied by Cambridge Isotope Laboratories.

Solid State NMR

^{13}C NMR spectra were recorded at 75.43 MHz and ^{29}Si NMR spectra at 59.58 MHz by the EPSRC NMR Service at Durham University. Both CPMAS and DPMAS experiments were performed.

CHN Microanalysis

Elemental analysis was performed by the University of St. Andrews Microanalysis Service on a Carlo Erba model 1106 elemental analyser.

FTIR Spectroscopy

FTIR spectra were recorded on a Perkin-Elmer 1710 spectrometer. The potassium bromide used to prepare KBr disks was supplied by Aldrich.

MALDITOF

Matrix assisted laser desorption/ionisation (MALDI) mass measurements were performed on a Micromass TOF Spec 2E mass spectrometer system equipped with a 337 nm N_2 laser and operating in positive ion reflection mode. Samples were dissolved in 1:1 ethanol-acetonitrile then prepared as an alpha matrix (α-cyano-4-hydroxycinnamic acid).

Surface Area Measurements

All surface area measurements were performed through the CATS catalyst evaluation and optimisation service. BET surface area measurements were made using a Micromeritics Gemini 2360 instrument using nitrogen at 77 K with adsorption being measured between P/P_0 values of 0.05 and 0.2. Full isotherms were collected using a Micromeritics ASAP2010 instrument, again using nitrogen at 77 K.

Powder XRD

Powder X-ray diffraction (PXRD) data were collected on a Stoe STADI/P transmission diffractometer, using Ge-monochromated CuKa1 radiation. Samples were mounted as a rotating disk between mylar films. Data were collected using a small position-sensitive detector covering about 6° in 2theta, with data points at 0.02° intervals.

HRMS

High resolution mass spectrometry (HRMS) was performed by the University of St. Andrews Mass Spectrometry Service on a VG (Fisons) Autospec equipped with double focusing and magnetic sector mass analyzer.

Melting Points

Melting points were obtained on a Gallenkamp Melting Point Apparatus.